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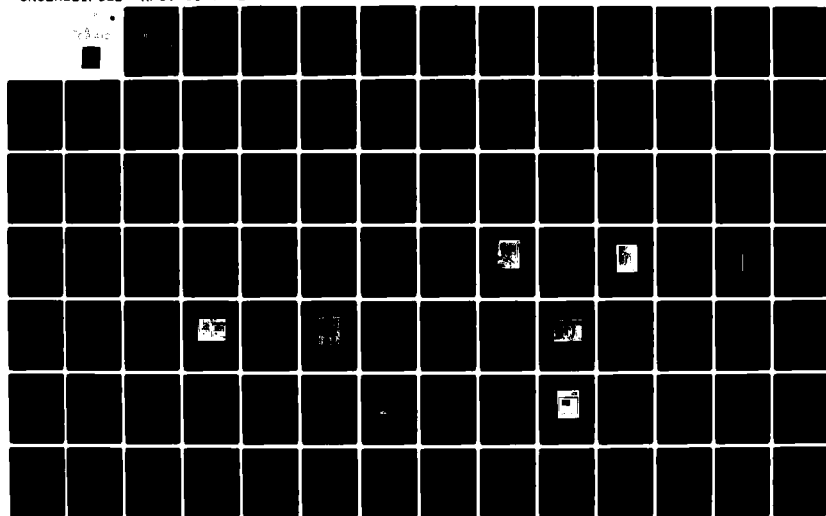
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ABSTRACT

Transportation vehicles' overall efficiency could be greatly increased if a hydrogen-air fuel cell served as the power source. Carrying hydrogen on board a vehicle presents immense weight and safety problems, however, and the fuel cell vehicle has so far been successful only in space or research study. Reforming of a source fuel into a hydrogen-rich gas offers a solution to the problems, especially if waste heat from the fuel cell can be used in the reforming. This paper discusses the ideas behind fuel cell vehicles, the choice of methanol as the source fuel and the detailed design and construction of a reformer system to test the possibilities. The reformer system is now operating at The University of Arizona, and early data has provided successful results. The system was designed to be reliable and capable of testing methanol reforming using variables of temperature, pressure, methanol to water ratio, carbon buildup, flow rate and differing catalysts. Early results predict that at temperatures of 400°F and below a larger catalyst volume may be required to produce the volume of hydrogen needed at fuel cell maximum power. Ethanol research is proposed.

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AN EXPERIMENTAL STUDY OF
METHANOL REFORMATION

by
John Bradford Shafer

A Thesis Submitted to the Faculty of the
DEPARTMENT OF ELECTRICAL ENGINEERING
In Partial Fulfillment of the Requirements
For the Degree of
MASTER OF SCIENCE
In the Graduate College
THE UNIVERSITY OF ARIZONA

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This thesis has been approved on the date shown below:

W. J. Kerwin
W. J. KERWIN
Professor of Electrical Engineering

Nov. 27, 1979
Date

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ABSTRACT

Transportation vehicles' overall efficiency could be greatly increased if a hydrogen-air fuel cell served as the power source. Carrying hydrogen on board a vehicle presents immense weight and safety problems, however, and the fuel cell vehicle has so far been successful only in space or research study. Reforming of a source fuel into a hydrogen-rich gas offers a solution to the problems, especially if waste heat from the fuel cell can be used in the reforming. This paper discusses the ideas behind fuel cell vehicles, the choice of methanol as the source fuel and the detailed design and construction of a reformer system to test the possibilities. The reformer system is now operating at The University of Arizona, and early data has provided successful results. The system was designed to be reliable and capable of testing methanol reforming using variables of temperature, pressure, methanol to water ratio, carbon buildup, flow rate and differing catalysts. Early results predict that at temperatures of 400°F and below a catalyst volume larger than 1.2 liters may be required to produce the volume of hydrogen needed at fuel cell maximum power of 2 KW. Ethanol research is proposed.

CHAPTER 1

INTRODUCTION

The United States, along with the rest of the world, faces an uncertain energy future of such proportions that not only can we expect a change in the standard of living, but more serious concerns of national security and survival must be considered. As Lawrence (1976, p. 1) notes, new energy conversion equipment must be developed which is efficient, economically attractive and environmentally sound. Part of that environmental question concerns the end result on our world, but part must be concerned with the very basic question of source availability. This paper cannot solve such problems, but this attempt to reduce or eliminate our dependence on petroleum products for transportation will certainly aid in the solution.

1.1 Hydrogen Economy

Hydrogen has been suggested (Reed and Lerner 1973, p. 1299) as a universal, non-polluting fuel. It is the ninth most plentiful element on our planet and is used as rocket fuel and in electricity generation already (Francis 1977, p. 42). Handling, shipping and safely using hydrogen, however, are such substantial negative factors that until recently it wasn't considered practical. Now the search for the hydrogen economy leads to fuel cells, and fuel cells lead to alternate fuels, such as methanol.

1.2 Fuel Cells

Fuel cells represent the only technology which converts fuel and air to electricity without the constraints of Carnot efficiency, and they have the potential of generating electricity with fuels ranging from hydrogen to coal to solid waste (Lawrence 1976, p. 1). Without considering the availability or polluting properties of any fuel, Table 1 shows the efficiencies of various alternatives for vehicular power (McCormick 1977, p. 28), and Figure 1 charts efficiencies at all levels of output (Wilk 1978, p. 35). If other factors are also considered, the fuel cell looks even better because it has a potentially high energy to weight ratio, no pollution and fuel flexibility which definitely favors the use of hydrogen (Lawrence 1976, p. 2). The factors which ruled out fuel cells in the past are rapidly disappearing, and cells are now being readied for commercial application (NASA 1975, p. 1). In fact, Los Alamos Scientific Laboratory (LASL) is currently testing a small fuel cell application on board a golf cart with plans to install it aboard a larger vehicle (Kerwin 1979, p. 1).

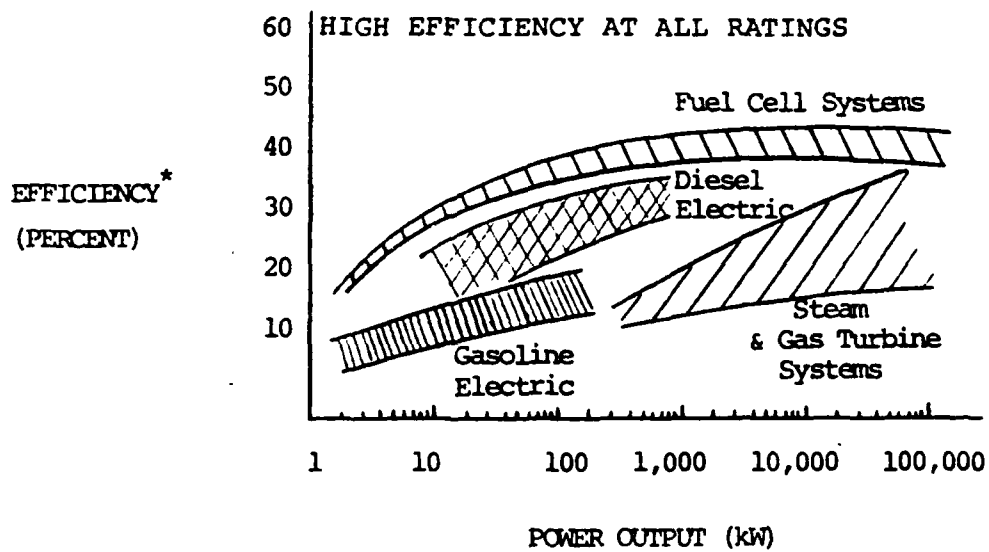
1.2.1 Background

In 1802, Sir Humphrey Davy suggested the idea of a fuel cell, and in 1839 Sir William Grove demonstrated a laboratory unit (Walsh 1967, p. 249). Fuel cell development was almost forgotten because of the rapid advance of the internal combustion engine and its readily available petroleum-based fuel. The space programs brought serious research back, and with declining petroleum supplies, the fuel cell

Table 1. Comparison of Efficiencies

	Subunit	Overall
Internal Combustion Engine		8.8%
Diesel Engine		9.9%
Battery-powered Electric		15.6%
Coal to Electricity	35%	
Transmission	85%	
Battery	70%	
Motor and Controller	75%	
Fuel Cell/Battery Hybrid Electric		18.4%
Coal to Methanol	70%	
Fuel Cell and Processor	35%	
Motor and Controller	75%	

Source: McCormick 1977, p. 28.



*BASED ON LOWER HEATING VALUE

Figure 1. Efficiencies of Systems -- Source: Wilk 1978, p. 35.

development programs are nearing installation of commercial units in electric utility power grids.

1.2.2 Operation

Basic equations governing fuel cell operation are shown in Figure 2 (Walsh 1967, p. 251), but the current state-of-the-art technology lies specifically with the acid-electrolyte system. Second generation technology lies with molten carbonate cells a few years into the future. Table 2 (NASA 1975, p. 36) lists a phosphoric acid cell's characteristics, and Figure 3 shows its operation (Lawrence 1977, p. 116). Figure 4 depicts a fuel cell stack, used to obtain the specific amount of power required, which would be used in modular form in vehicles (Hoover 1979, p. 44). Tests on the fuel cell stack at LASL show that an 88 cell stack will put out 77.5 volts at 0.0 amps and about 40 volts at 70.0 amps (Kerwin 1979, p. 1). Further, operation at 10 amps requires 6.8 liters of hydrogen per minute, and at 70 amps it takes 49 liters per minute (Kerwin 1979, p. 1). Because of that hydrogen requirement we are apparently back to the storage problems of a hydrogen economy.

1.2.3 Hydrogen Supply

The problem of hydrogen storage has been a major stumbling block to the introduction of the hydrogen engine, whether fuel cell or augmentation of a normal internal combustion device. Three storage concepts studied over the last few years are high-pressure gas, cryogenic liquid and metal hydride. Though metal hydride storage

FUEL CELLS

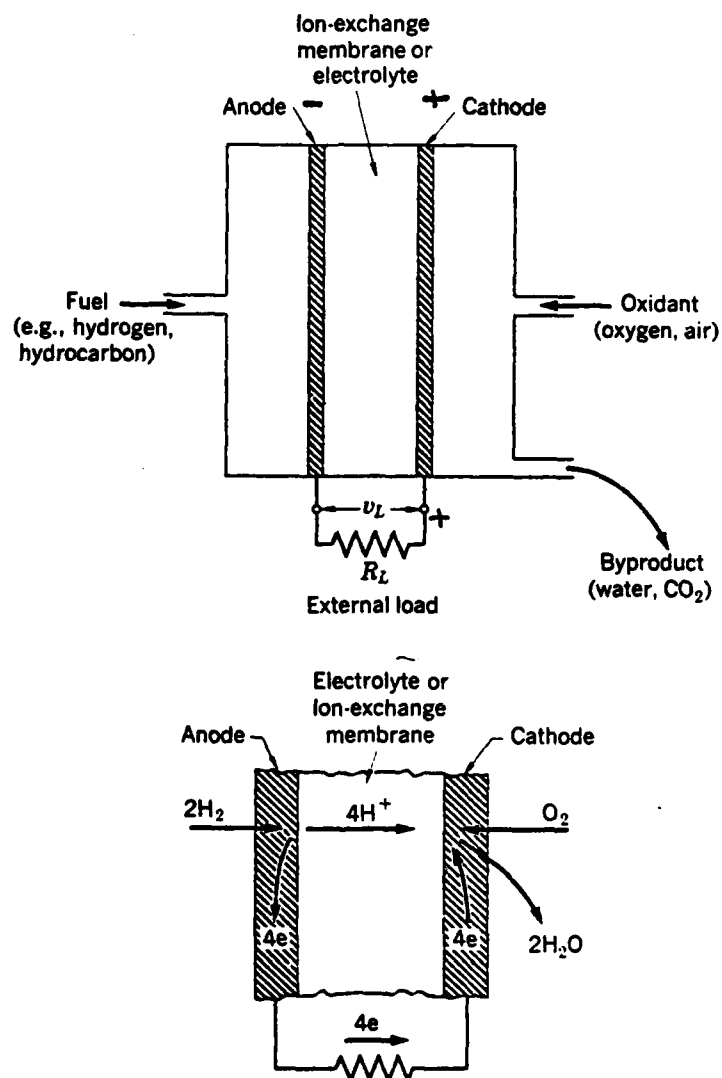
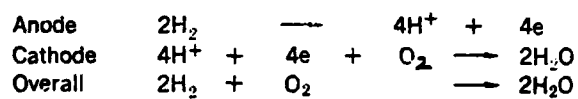


Figure 2. Typical Fuel Cell -- Source: Walsh 1967, p. 251.

Table 2. Phosphoric Acid Cell Characteristics

Prototype Demonstration Date:	1980
Production Quantities Price per KW:	\$350 (1975 dollars)
Lifetime:	20 years
Between fuel cell overhauls:	40,000 hours
Between fuel processor overhauls:	80,000 hours
Fuels:	Naptha, natural gas, hydrogen
Emissions:	Below federal standards
Cooling:	Air or water
Water:	No makeup required

Source: NASA 1975, p. 36.

HOW THE FUEL CELL WORKS

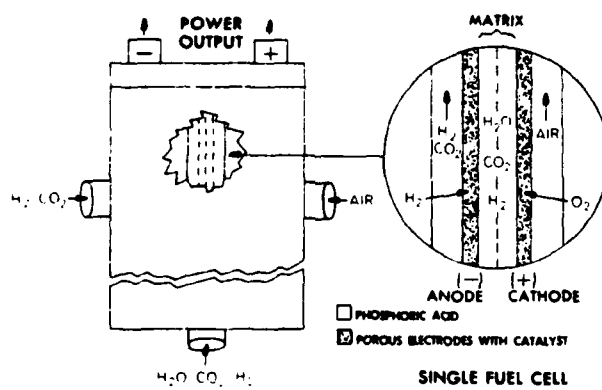


Figure 3. How a Phosphoric Acid Fuel Cell Works --
Source: Lawrence 1977, p. 116.

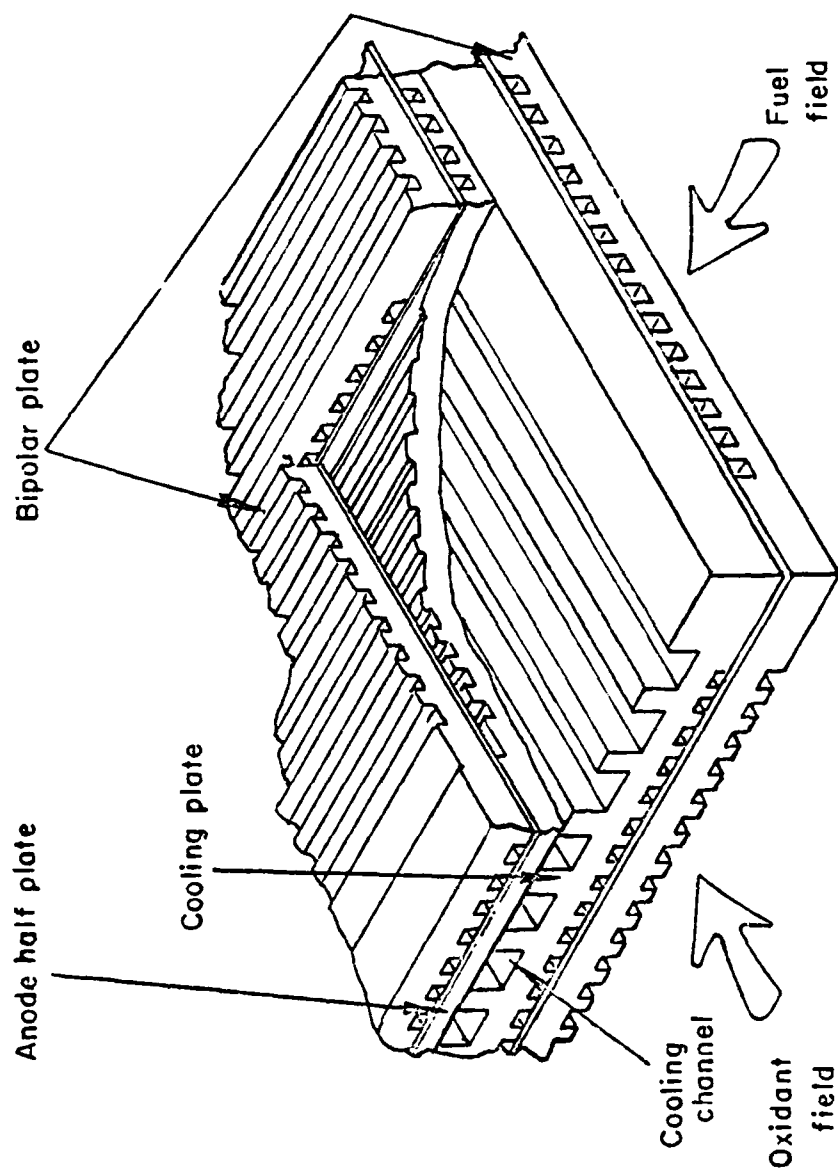


Figure 4. Typical Fuel Cell Stack -- Source: Hoover 1979, p. 44.

looks promising in the long term, near term use of any of these presents high weight penalties, container problems and/or material selection problems (Kester, Konopka and Camara 1975c, p. 1). An alternate concept which has been partially studied is the storage of hydrogen as a reactive mixture of methanol and water which is vaporized and catalytically converted into a hydrogen rich gas on demand (Kester and others 1975b, p. 1). Such a fuel supply might have considerable output fluctuations, but as Figure 5 shows, cell operation is not greatly affected by a changing fuel mix (Gillis, Kezer and Taschek 1970, Fig. 4).

1.2.4 Alternate Fuels

The Aerospace and Mechanical Engineering Department (Martin 1977, p. 2) determined that the desirable characteristics of a vehicular fuel system included:

1. Liquid form -- to use existing distribution facilities.
2. Burnable in internal combustion engines with only minor modifications to existing designs.
3. Emission levels below EPA standards.
4. Increased efficiency.
5. Initial operation with current fuels as an additive or in parallel system of distribution, but capable of full conversion to an alternate fuel as the alternate supply increases and the current fuel disappears.

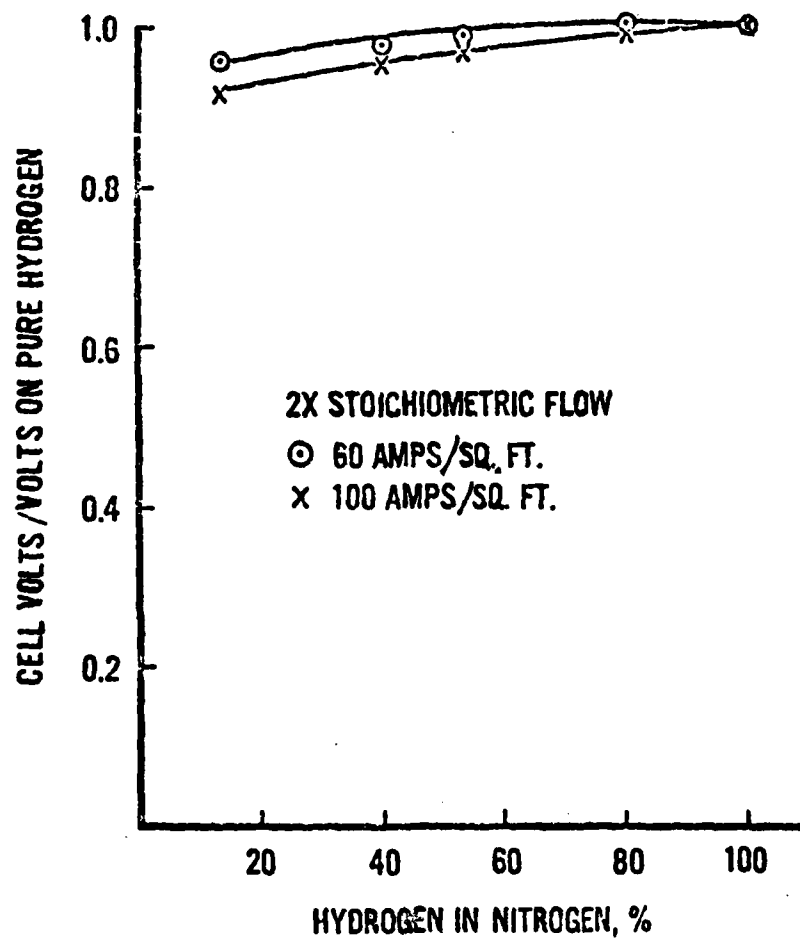


Figure 5. Fuel Cell Operation on Dilute Fuel -- Source: Gillis, Kezer and Taschek 1970, Fig. 4.

Considering those ideals, Tables 3 and 4 (Reed and Lerner 1973, pp. 1301-1302), Tables 5 and 6 (Gillis, Pangborn and Vyas 1975, pp. 859-860), Table 7 (Kester and others, 1975a, p. 12) and Figure 6 (Reed and Lerner 1973, p. 1300) show how methanol compares to other alternatives. In addition, the production of methanol from syngas is a proven commercial technology, and the syngas can be coal-derived (Wilk 1978, p. 56). The disadvantages of methanol concern the fact that more will have to be carried than gasoline for the same energy output and that this problem is increased by a need to mix water with the methanol if it is to be used in a catalytic reforming process. The water problem is not as bad as it seems; according to Kurpit (1975, p. 226) the fuel consumption of his methanol powered 1.5 kw generator measured in gallons per hour was equal to the consumption of the standard gasoline-driven unit, despite the fact that the methanol fuel contained 45.67% water by weight. The total tank requirement will still impose a small penalty on methanol fuel when compared to gasoline, but when other factors are considered, that disadvantage pales. Reed and Lerner (1973, p. 1299) note that methanol can be made from natural gas, petroleum, coal, oil shale, wood and municipal wastes. It is easily stored in conventional tanks, can be transported by the already existing system, and it can fit directly into the distribution and marketing system for automotive fuels without forcing the duplication of the multibillion dollar investment already in place (Farmer 1975, p. 863). Methanol meets all five of the desirable characteristics previously mentioned for use as a

Table 3. Alternate Fuel Production Costs -- 1973 figures.

Fuel	Source	Cost	
		\$/10 ⁶ Kjoule	\$/10 ⁶ Btu
Gasoline	Crude Oil	1.00	1.05
Methanol	Natural Gas	1.49	1.57
	Coal	1.40	1.48
	Lignite	1.18	1.24
Methane Gas	Wellhead	.14-.37	.15-.39
	Imported LNG	.76-.95	.80-1.00
	Coal	.76-.95	.80-1.00
Hydrogen Gas	Natural Gas	.92	.97
	Coal	1.25	1.32
Liquid Hydrogen		2.37	2.50

Source: Reed and Lerner 1973, p. 1301.

Table 4. Alternate Fuel Storage and Transportation Costs

Fuel	Cost, \$ per 10 ⁶ Btu	
	Storage	Transport 100km
Gasoline	2.11- 15.82	.02
Methanol	3.16- 22.15	.03
Gaseous Hydrogen	369.20	.04
Liquid Hydrogen	316.45-1,054.85	1.64

Source: Reed and Lerner 1973, p. 1302.

Table 5. Tank Requirements for Alternate Fuels^a

Fuel	Formula	LHV, Btu/lb	Tank, gal	Full Tank, lb
Ammonia	NH_3	8,000	45	385
Methanol	CH_3OH	9,080	45	165
Coal	C	10,000	18	200
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	11,920	30	235
Gasoline	Mix	19,290	22	145
LPG	C_3H_8	19,940	27	180
Methane, 1	CH_4	21,250	45	165
Hydrogen, 1	H_2	51,620	105	200

a. All tank values are based on the energy equivalent of 20 gallons of gasoline.

Source: Gillis, Pangborn and Vyas 1975, p. 859.

Table 6. Problem Areas of Alternate Fuels

Fuel	Vehicle Tank	Engine Compatible	Distrib. System	Resource Available	Fuel Toxicity
Ammonia	X ^a	XX ^b	XXX+ ^{c,d}	X	XX
Methanol	X	X	X	X	X
Coal	XX	XXX+	XX	X	X
Ethanol	X	X	XX	XX	X
Gaoline	X	X	X	X- ^e	X
LPG	X	X	XX	X-	X
Methane, 1	XX	X	XX	X-	X
Hydrogen	XX+	X	XXX+	X	X

a. X -- No great difficulty

b. XX -- Some difficulty

c. XXX -- Serious difficulty

d. + -- Long term better

e. - -- Long term worse

Source: Gillis, Pangborn and Vyas 1975, p. 860.

Table 7. Component Weight and Volume Penalties

	Weight, Lb	Volume, Cu Ft
<u>Components:</u>		
Methanol, Water and Tank	400	7.2
Vaporizer and Reactor	250	2.4
Catalyst	100	In Reactor
Pump, Plumbing, etc.	<u>25</u>	<u>0.3</u>
	775	9.9
<u>Reference:</u>		
20 gal Gasoline and Tank	142	2.8
<u>Penalty:</u>		
	775-142=633	9.9-2.8=7.1

Source: Kester and others 1975a, p. 12.

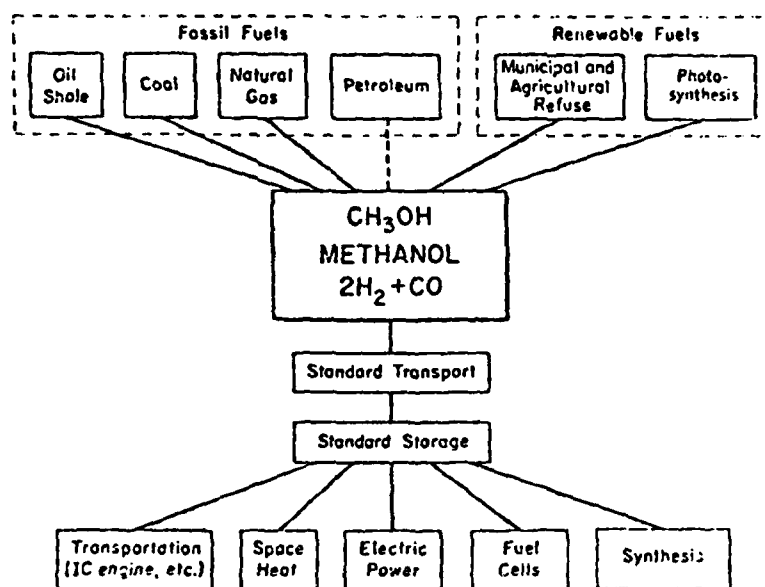


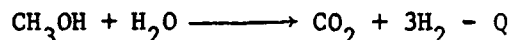
Figure 6. Sources, Transport and Uses of Methanol -- Source: Reed and Lerner 1973, p. 1300

direct fuel in internal combustion engines, yet it is also one of the few known fuels suited to power fuel cells (Reed and Lerner 1973, p. 1301). Thus, methanol is selected as the most promising replacement for gasoline in our transportation system, whether the focus is toward existing internal combustion engines or fuel cells. Table 8 (Stinson 1979, p. 28) summarizes the important qualities of methanol.

1.2.5 Methanol Reforming

Because this paper is concerned with developing the most efficient future power source, rather than the phase-out of the internal combustion engine, the focus from this point on will be toward the steam reformation of methanol to provide a hydrogen-rich fuel to power a vehicle-mounted fuel cell.

The basic reaction governing the production of hydrogen from methanol is:



This occurs by sending a 1:1 molecular ratio of methanol and steam over an appropriate catalyst at a temperature from about 400°F up to 1000°F. In addition to carbon dioxide and hydrogen, the gaseous product contains a small amount of carbon monoxide from the reaction:



The amount of carbon monoxide varies with the operating conditions (catalyst, temperature, flow rate, methanol/water ratio and pressure) and is usually between 0.1 and 2.0% (Prigent, Dezael and

Table 8. Methanol at a Glance

Structure:	CH_3OH
Weight vs. Volume:	0.7914 kg per liter 6.604 lb per gallon 302.8 gal per ton
Energy Content:	66,700 Btu per gallon
Price (1979):	\$0.46 per gallon \$6.90 per million Btu
Production:	1.1 billion gallons in 1979
Capacity:	1.25 billion gallons per year
Producers:	Air Products, Borden, Celanese, DuPont, Georgia Pacific, Hercofina, Monsanto, Rohm & Haas, Tenneco, Valley Nitrogen
Boiling Point:	148.5 °F
Density:	0.792 gram per cm ³

Source: Stinson 1979, p. 28.

Breelle 1970, p. 5-111). Under some conditions the product mix will also contain methane (CH_4), water and unreacted methanol. Methane is inert in the fuel cell and carbon dioxide passes through into the exhaust, but carbon monoxide acts as a poison to the cell and must be kept at an absolute minimum. From a chemical point of view, the methanol/water ratio need only be 1:1, the stoichiometric requirement. At that ratio, all of the methanol and all of the water can be consumed. Excess water will result in unreacted water in the product but can provide lower levels of carbon monoxide and a higher conversion percentage for the methanol (Kester and others 1975b, p. 4). In addition, excess water helps prevent carbon buildup on the catalyst and thus prolongs catalyst life (Hoover 1979, p. 45). Methanol/water ratios where water is greater than 1 (for example, 1:1.3) begin to add weight to the system because more water must be carried, however, so an optimum operating point must be found. Temperature variation has similar effects; the phosphoric acid cell operates up to about 400°F so lower reforming temperatures become necessary if fuel cell waste heat is to heat the reformer, but at lower temperatures less of the methanol may be reacted. Thus the need for research.

1.2.6 Research Required

The hydrogen economy requires an alcohol-type fuel to make it practical.

We are all very familiar with the demands of the automotive industry upon the petroleum resources of the world . . . but the greatest affect this abnormal demand has created is

reflected in the price per gallon of gasoline which in the United States has quadrupled in the last 10 years. In our opinion, the use of alcohol as a fuel is bound to come eventually in the U.S. There are in the U.S. yearly millions of tons of unused vegetable matter from which alcohol could be profitably manufactured. If the automotive industry will demand the manufacture of alcohol for fuel purposes, it will head the list of automotive fuels eventually (Gonnerman, Moore and McCallum 1975, p. 850).

That quote was from a Society of Automotive Engineers paper by A. W. Scarratt and should come as no shock except that the Scarratt paper was presented in 1921! We must get on with the research; although much has been done, it is not conclusive. For example, Figure 7 (Baker 1977, p. 48) indicates that favorable conditions for reforming methanol exist at temperatures below 400°F, that CO content is greater than 1.0% at 400°F, and that the H₂% doesn't change from 360 to 420°F. Figure 8 (Dixon, Houston and Johnson 1972, p. 1085) agrees on some points but shows CO content greater than 2% at 400°F, and H₂% decreasing with temperature. Figure 9 (Kester and others 1975c, p. 56) shows CO below 0.5% at 400°F, and H₂% increasing with temperature. Figures 10 and 11 (Kester and others 1975c, p. 61) clarify the situation somewhat by depicting unreacted methanol and water, and Table 9 (Kester and others 1975b, p. 5) shows a decrease in H₂% as the amount of water is increased. Figure 12 (Bertrand 1979, p. 54) predicts, from equilibrium conditions, that CO will be negligible, H₂ less than 5%, and CH₄ greater than 70% in the dry product gas at 400°F. Such a mix of predictions and "typical" results, when added to the fact that individual system characteristics govern the kinetics of the reactions, makes it mandatory that actual results be

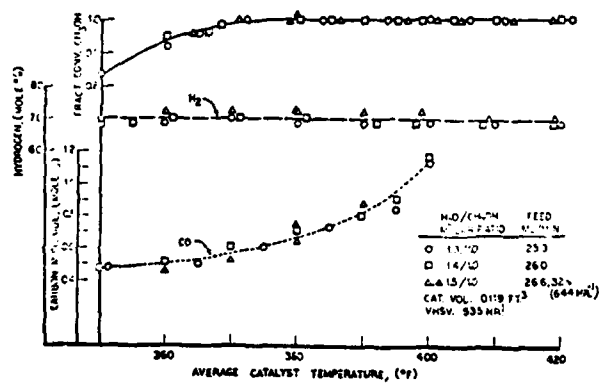


Figure 7. Methanol/Steam Reforming Products (Typical) -- Source: Baker 1977, p. 48.

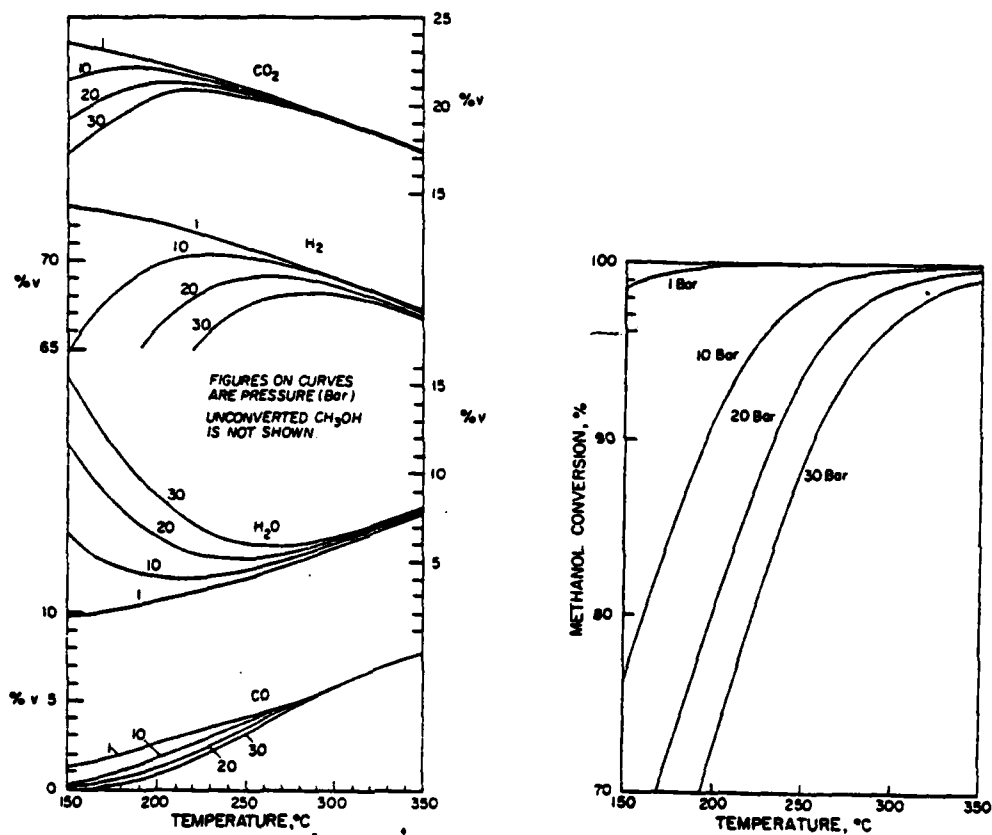


Figure 8. Methanol/Steam Reforming Products (Shell) -- Source: Dixon, Houston and Johnson 1972, p. 1085.

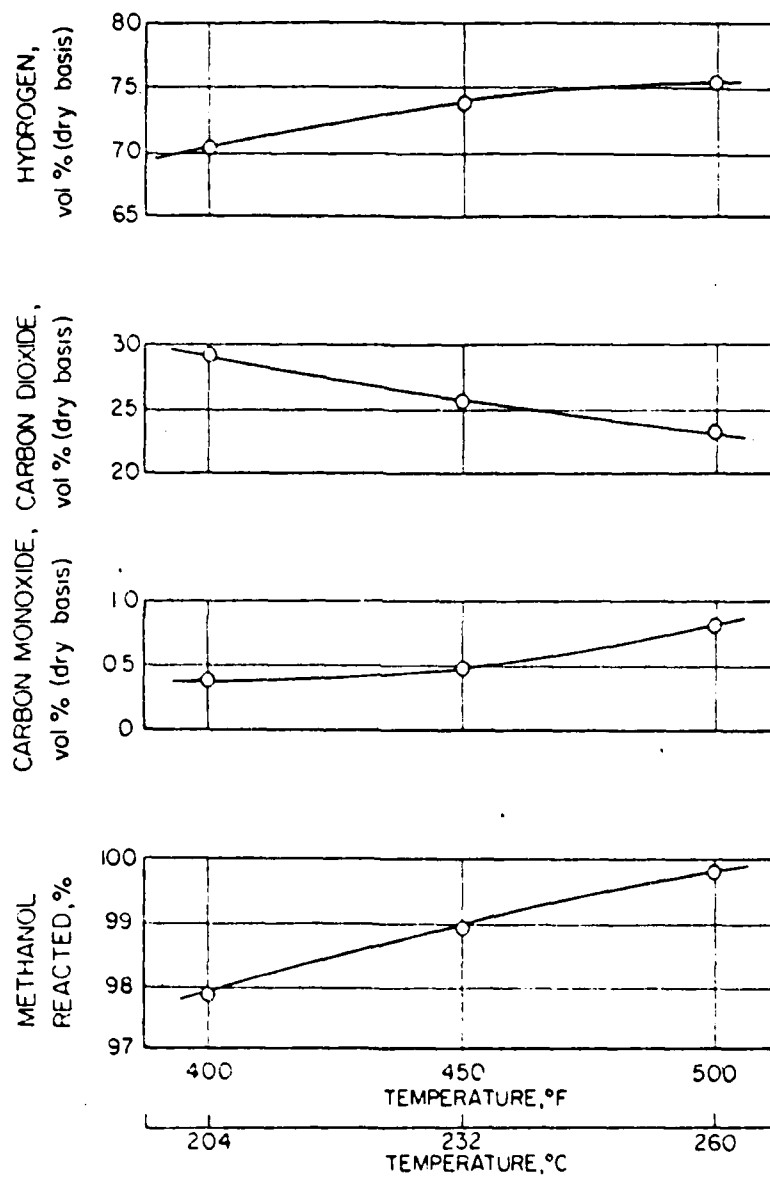


Figure 9. Methanol/Steam Reforming Products (IGT) -- Source: Kester and others 1975c, p. 56.

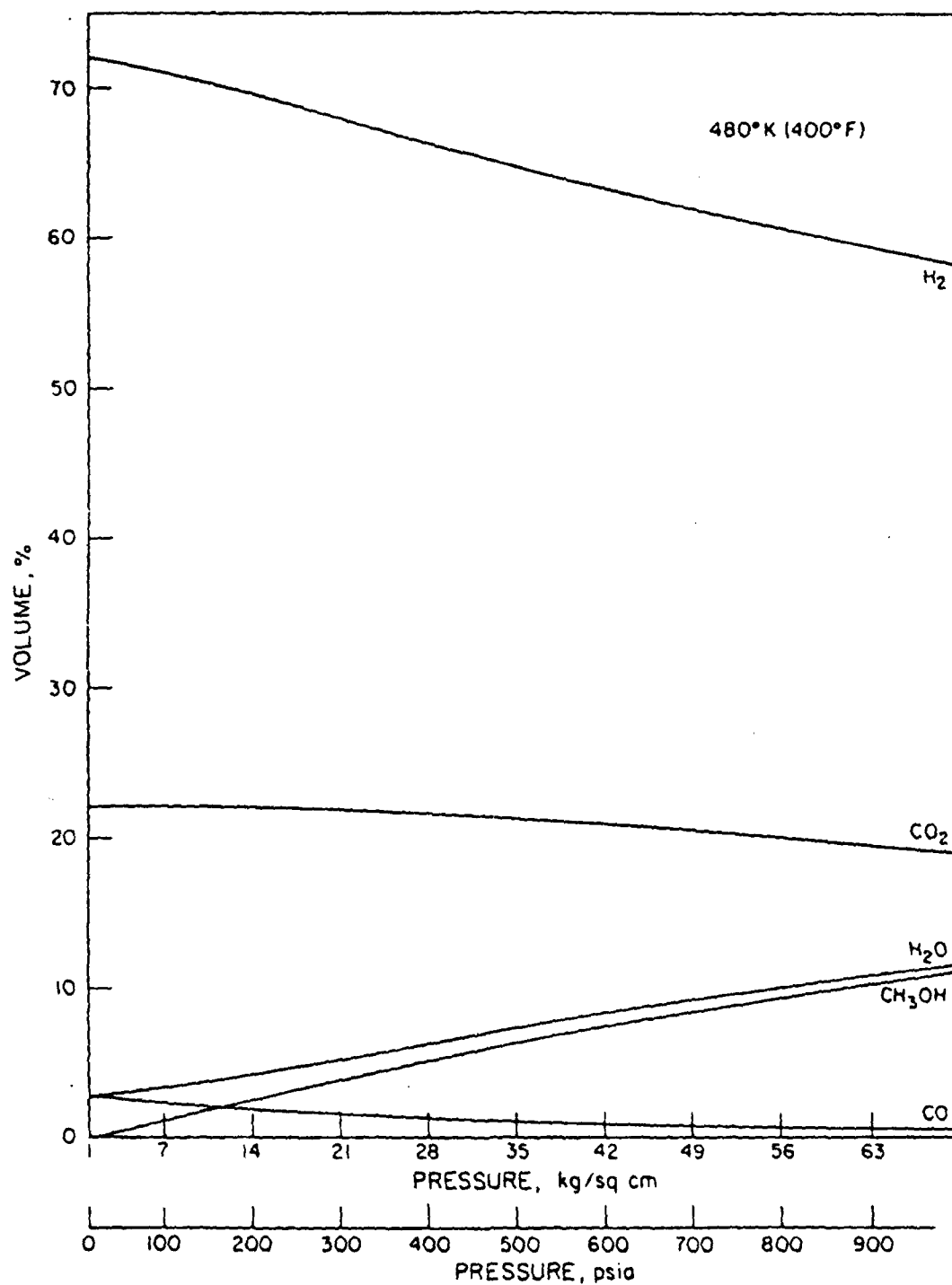


Figure 10. Methanol/Steam Reforming Products at 1:1 Ratio and 400°F
-- Source: Kester and others 1975c, p. 61.

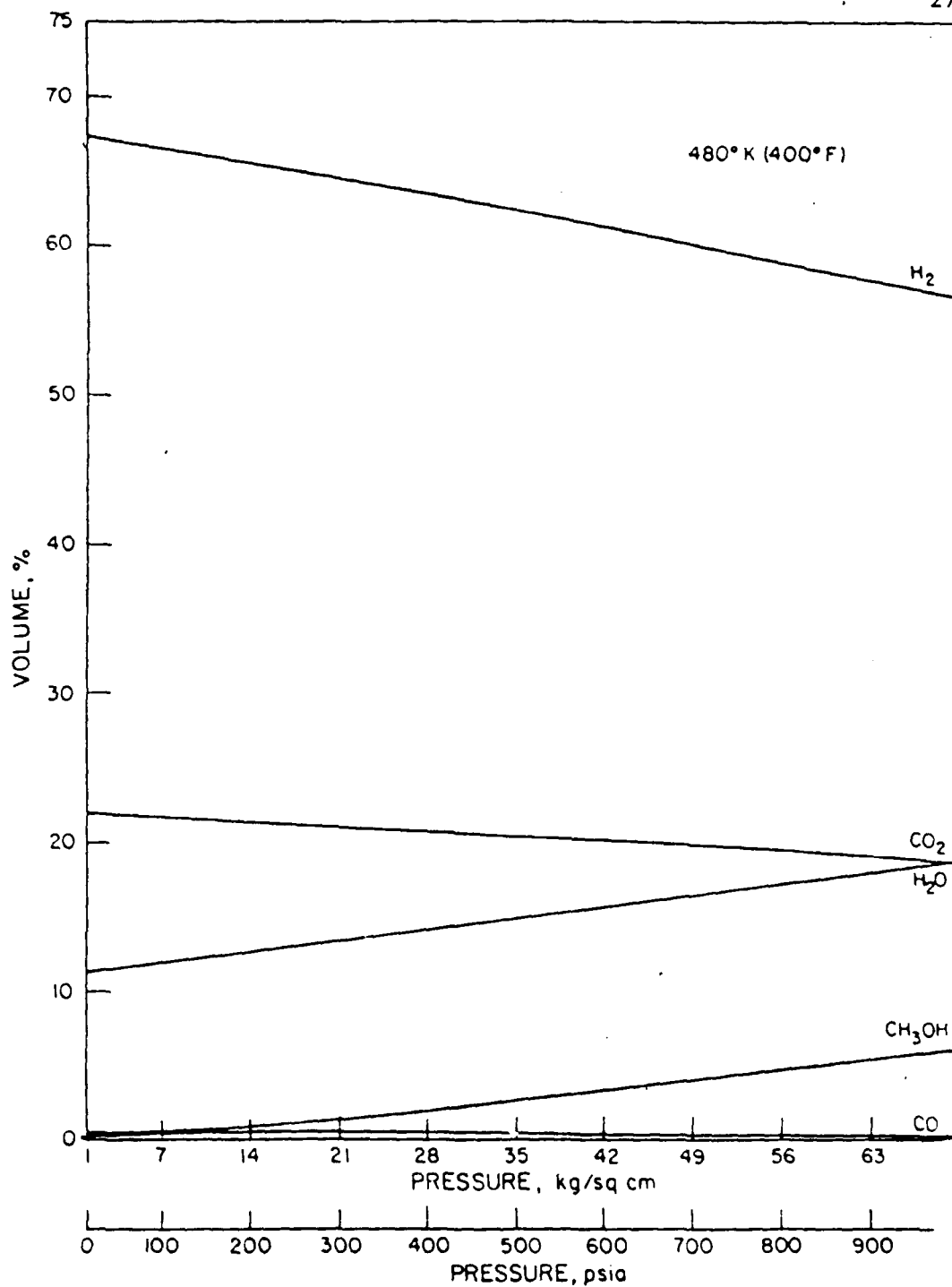


Figure 11. Methanol/Steam Reforming Products at 1:1.5 Ratio and 400°F -- Source: Kester and others 1975c, p. 61.

Table 9. Effect of Methanol/Water Ratio

CH ₃ OH/H ₂ O Mole Ratio		Composition of Products	
		kg-moles	Volume %
1:1.0	H ₂	1.296	71.4
	CO ₂	0.389	21.4
	CO	0.065	3.6
	H ₂ O	0.065	3.6
1:1.1	H ₂	1.313	70.5
	CO ₂	0.406	21.8
	CO	0.049	2.6
	H ₂ O	0.093	5.0
1:1.2	H ₂	1.324	69.5
	CO ₂	0.417	21.9
	CO	0.036	1.9
	H ₂ O	0.093	5.0
1:1.3	H ₂	1.332	68.3
	CO ₂	0.425	21.8
	CO	0.029	1.5
	H ₂ O	0.165	8.5
1:1.4	H ₂	1.337	66.9
	CO ₂	0.430	21.5
	CO	0.024	1.2
	H ₂ O	0.205	10.3
1:1.5	H ₂	1.341	65.7
	CO ₂	0.434	21.3
	CO	0.020	1.0
	H ₂ O	0.247	12.1

Source: Kester and others 1975b, p. 5.

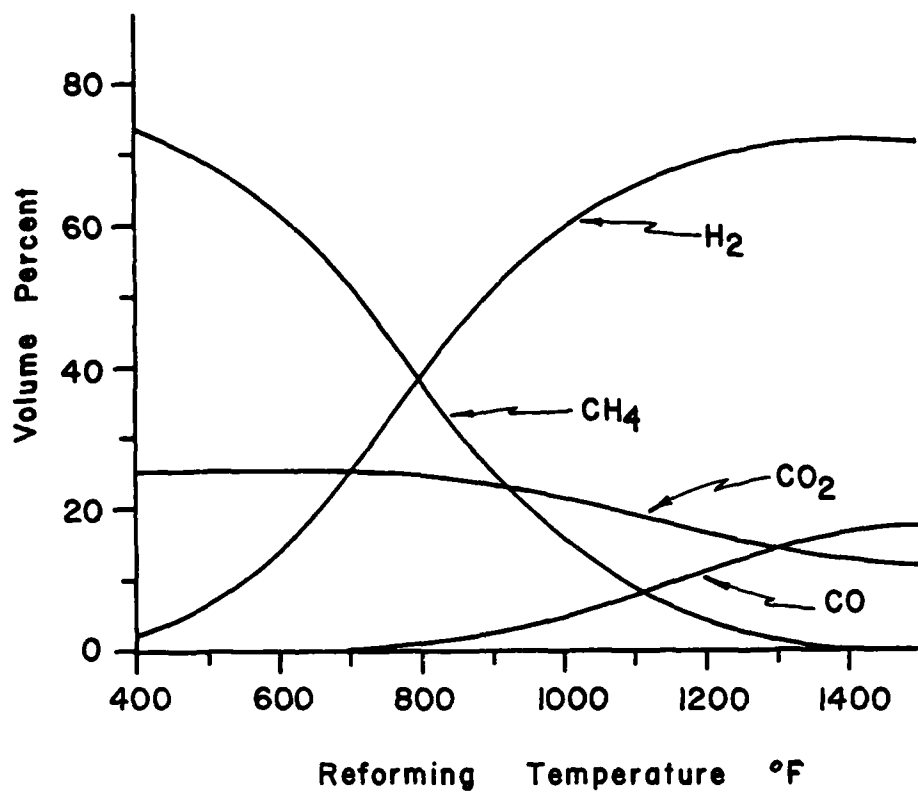


Figure 12. Methanol/Steam Reforming Products at 1:2 Ratio and Equilibrium -- Source: Bertrand 1979, p. 54.

tabulated on a single system where the effects of varying temperature, pressure, flow rate, catalyst and methanol/water ratio can be carefully evaluated before making decisions on a vehicle-compatible system. Additional need for such a system is indicated in the Department of Energy (DOE) Program Research and Development Announcement (Dawkins 1979, p. 1) when it states that DOE is requesting research proposals in hydrocarbon reforming for hydrogen fuel cells. The AME Department planned a response to this announcement based on having a test reformer system which could evaluate all the variables. As of October 18, 1979, that system is fully operational and the remainder of the paper describes its design, construction and early results.

CHAPTER 2

REFORMER SYSTEM DESIGN

The design had to provide the capability to evaluate the following variables:

1. Temperature -- especially whether or not methanol could be effectively reformed at 400°F or below so that fuel cell waste heat could supply the required heat.
2. Pressure -- effect of low pressures, near atmospheric, on the reformed product makeup, because low pressure systems would be easiest to install in a vehicle.
3. Flow Rate -- to determine what volume of catalyst is required to produce enough hydrogen to power a vehicular fuel cell.
4. Catalyst -- to evaluate available types to determine which is most efficient at the temperature, pressure and flow rate compatible with vehicular fuel cells.
5. Methanol/water Ratio -- to find the ratio closest to the ideal 1:1 which prevents carbon buildup on the catalyst and excessive carbon monoxide in the product. The lowest possible amount of water will reduce the weight penalty in a vehicular application.

2.1 Previous Designs

The University of Arizona has had some type of on-going research in this area at least since 1973 when Gregory A. Lorton (1973) submitted his thesis, "Steam-hydrocarbon Reforming for Lower Polluting Automotive Fuels" to the Chemical Engineering Department. The direction of research in the early years was mainly toward reducing pollution and accepting increased efficiency as a by-product. The AME Department has had at least three reformers constructed. The first was heated electrically using Lindberg radiant heating units with large variacs to control temperature. This system was discarded in favor of a reformer heated by an aircraft-type gasoline-powered space heater designed in 1977 by Vernon O. Willan (1977). The heater was mounted too close to the catalyst bearing reformer tubes, however, and the reformer was burned by flame impingement. A third reformer was designed by W. Leonhart (Willan 1977, p. 8) to support the Department's interest in hydrocarbon reforming to provide hydrogen augmentation (or full operation) to a laboratory Volkswagen engine. Plans called for this system to be refined to fit into the Department's Pinto Fuel Research Vehicle as definitive results were obtained. Numerous problems, including "frequent breakdowns" (Scott 1979, p. 3), "electronic bugs" (Martin 1977, p. 4), "shipping delays" (Willan 1977, p. 23) and "heat transfer difficulties" (Bertrand 1979, p. 1) added to the complexities of running the system with the Volkswagen engine and no reliable data was obtained. In May 1979, Professor Kerwin of the Electrical Engineering (EE) Department joined forces with Dr.

Scott of the AME Department and formed a pool of students to redesign the system and make it operational. Louis Bertrand became the advising engineer and thermochemistry evaluator. Howard Silverman accepted responsibility for the new data system. Susan Hyde did the thermodynamic analysis. I became the system electronics engineer, and ultimately, the "production engineer" in charge of overall design and construction. Jim Blair joined the project in September 1979 as an experienced product sampler and is phasing into the chief engineer's job to continue research and upgrading into 1980.

2.2 Design Parameters

The following limitations were placed on the new system design during meetings of the project members:

1. It must be reliable.
2. It must allow "universal" application so that both AME and EE goals could be met.
3. It must be built using as much existing equipment as possible because no grants were available.
4. It must be compatible with the AME Department's new Hewlett Packard Data System which was still on order during preliminary phases of design.
5. It must provide the capability to evaluate all the variables listed at the beginning of this chapter.

Figure 13 shows a basic block diagram of the system plan and Figure 14 is a top-view schematic of the reformer project's main subsystems as they stood on the first operational run October 18, 1979.

2.3 Subsystem Designs

Each part of this section describes the design and construction of a main subsystem both as a report of my work and as a much needed "catalog" of data for future reference when questions arise about the design.

2.3.1 External Heat Side

Elements include the Willan/Reid Burner, Reformer Heat Side, Superheater, Evaporator, Exhaust System and the connections between elements.

2.3.1.1 Willan/Reid Burner. The burner provides the heat needed for reforming (see Figure 15). The first problem to be solved was the elimination of flame impingement on the reformer while allowing better temperature control and measurement. This was accomplished by cutting the angle out of Willan's previous design (Willan 1977, p. 18) and welding on a 3" diameter stainless steel tube 48" long. A 6" section of 2" pipe was then welded onto that to provide the male pipe threads which mate with the reformer heat input side. Thermocouple fittings were mounted on the output end of the burner and near the original air input. A secondary air input was tangentially mounted to the stainless steel extension to allow additional air for flame temperature control. Total air flow, primary air and secondary

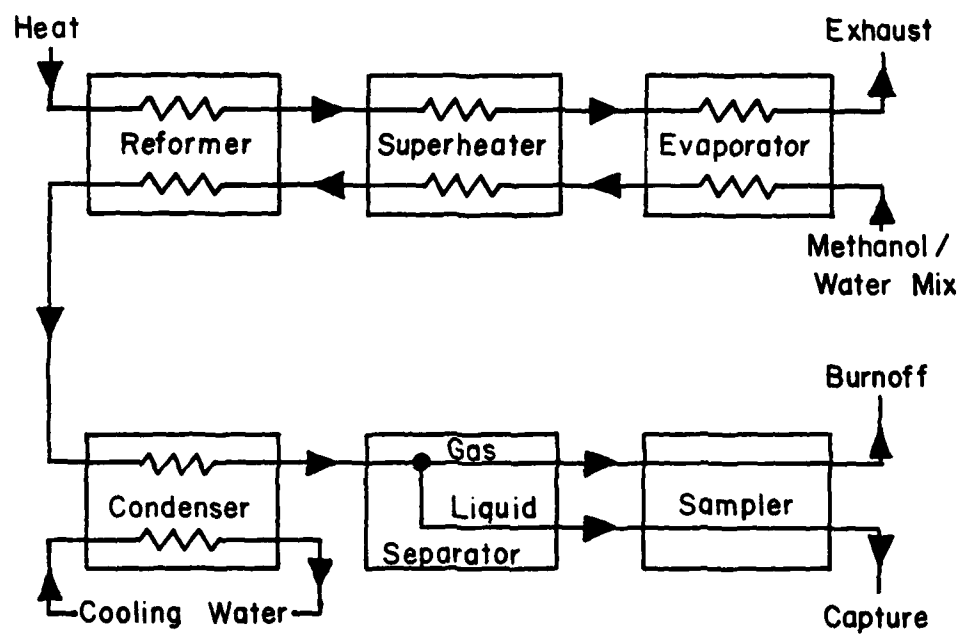


Figure 13. System Block Diagram

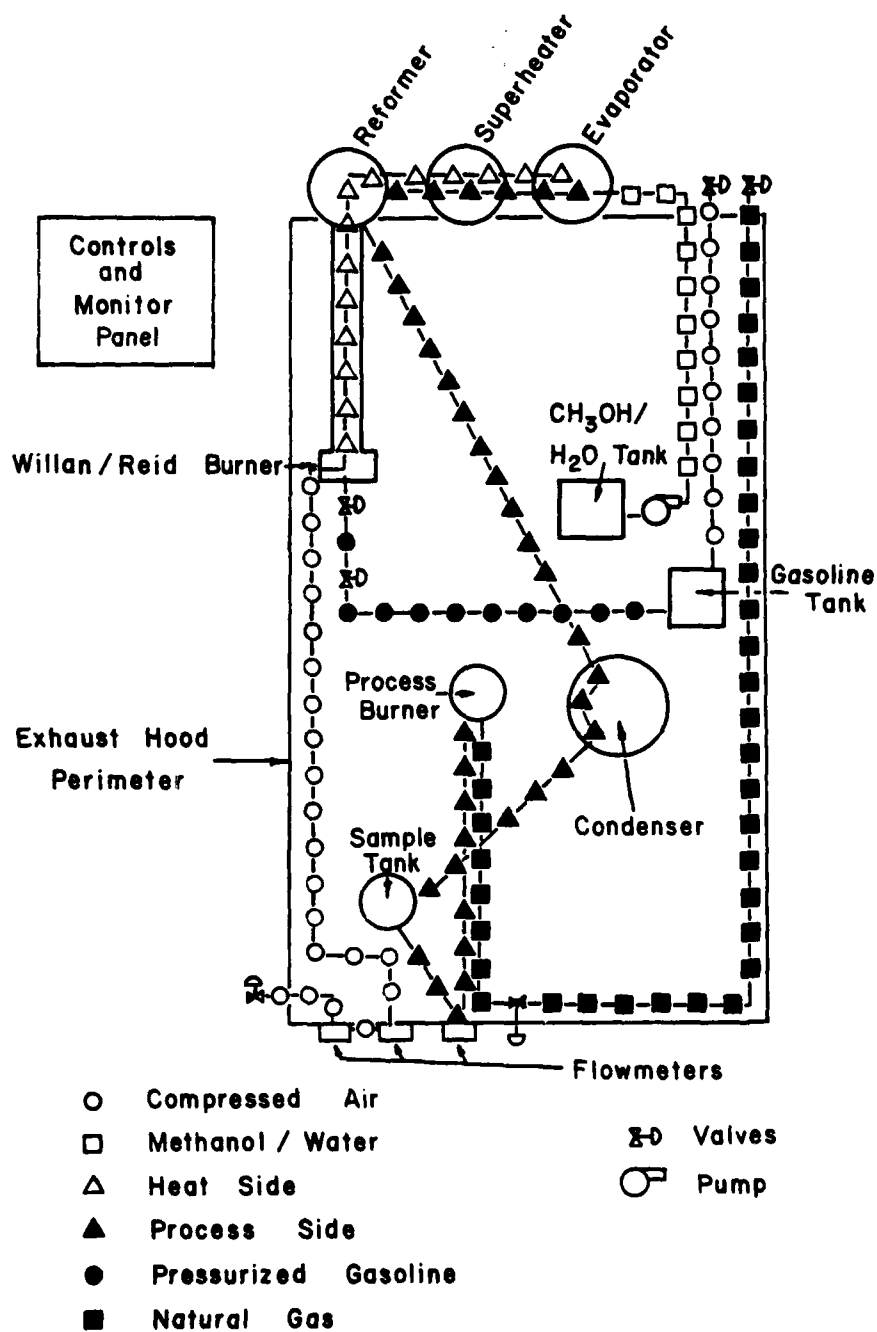


Figure 14. System Top View Schematic

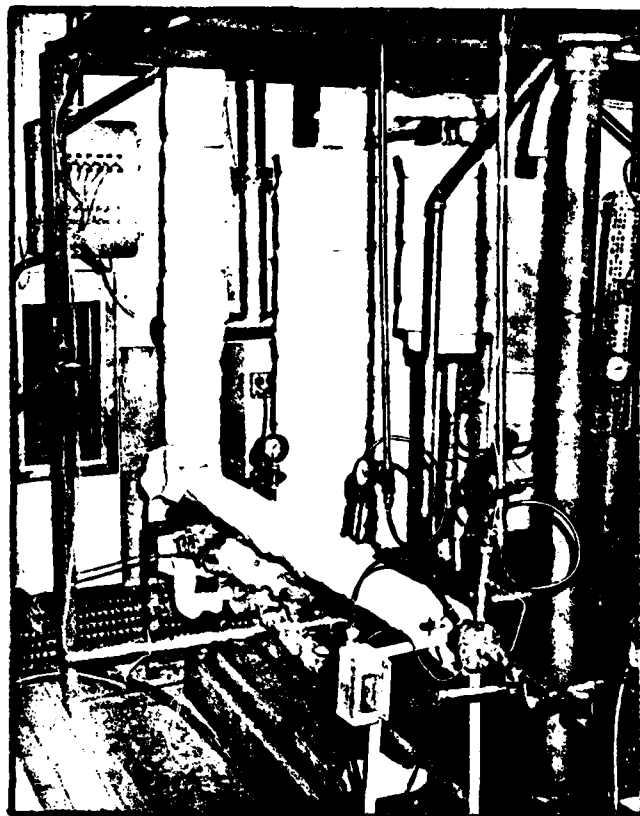


Figure 15. Willan/Reid Burner and Reformer

air were controlled through the flow metering panel shown in Figure 16. The flowmeters in use in October 1979 were Fisher and Porter models rated at specific gravity of 1.0, 14.7 psia and 70°F, as listed below:

- | | | |
|------------------|-------------|-----------|
| 1. Total Air | 6107A1601B4 | 169 SCFM |
| 2. Primary Air | 6107A1601B2 | 31 SCFM |
| 3. Secondary Air | 6208A2550B1 | 6.25 SCFM |

The first two digits of the serial number indicate the year of purchase, so already existing equipment was definitely used. A tangential flow air dryer was added in the compressed air line prior to the flowmeters, and a regulator followed it to smooth out pressure variations caused by the automatic on/off function of the air compressor. The compressor was already installed in the lab and had a steady flow capability of about 140 lbs/hr at 39 psig. It was manufactured by the Kellogg Division of American Brake Shoe Company and carried model number B 351 A0. The main lines of this system were of 1/2" copper tubing.

The Willan/Reid burner was fueled with pressurized gasoline. There was safety concern over such an arrangement, but a similar system had been used previously and no better equipment was readily available. The gasoline tank had a 2-1/2 gallon capacity and was pressurized by a 1/4" copper tubing line from the main air supply through a shutoff valve and pressure regulator. The line from the tank to the burner was also 1/4" copper tube and had another shutoff valve, an AC glass-bowl fuel filter and a C6 Gould 110 VAC solenoid

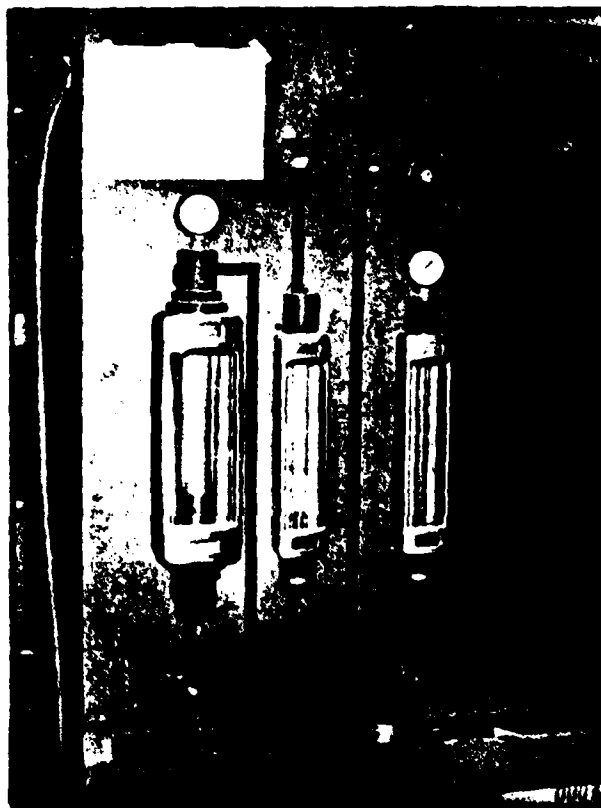


Figure 16. Flow Metering Panel

shutoff prior to entering the burner. The fuel used was unleaded gasoline from the University garage.

The Willan/Reid burner was lit using a Bendix Ignition Exciter, type TCN-1015, which necessitated a DC power supply capable of up to 30 volts and 5 amps. A Kepco 5 amp supply was located, tested and installed in the control panel. The igniter had a duty cycle which left it off 27 minutes out of 30 so once light-off was assured, the igniter was turned off, but the power supply was left on in case of a flameout. Tests also required an extra grounding wire between the igniter and burner to prevent arcing from the burner stand to the metal floor. Toggle switches (SPST) on the panel controlled both the fuel shutoff solenoid and the igniter.

The Willan/Reid burner nozzle was a South Wind aircraft heater, part number 714710, and was rated at 1/2 gallon per hour at 7 psig. Our tests showed a rate of use very near that though operating pressures ranged from 3 to 15 psig. For more details of the burner's original design, see Willan's report (1977, p. 11). The burner was re-christened as a Willan/Reid burner after Jordan Reid completed the extensive modification necessary to make it more useful.

2.3.1.2 Reformer -- Heat Side. The reformer uses heat from the Willan/Reid burner, passing over sealed tubes (containing catalyst and the process gas of methanol/water mix), to provide the necessary heat for reforming. The heat and process sections are sealed against leaks and the opposite-direction flows remain totally separate (see Figure 17). The reformer is 84" tall and mounted on an 18"

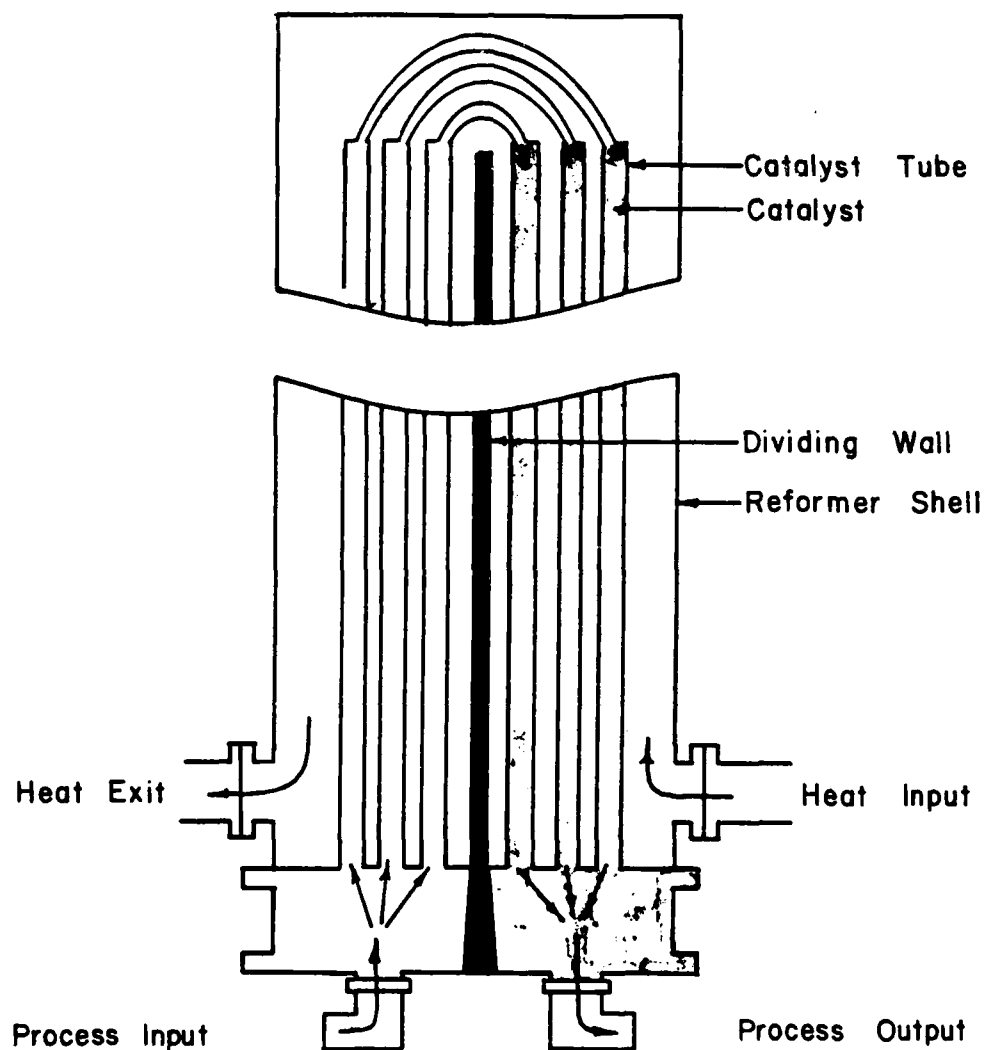


Figure 17. Reformer Cross-section

base to permit attachments and piping to be fitted at the bottom. The stainless steel process tubes are 1" diameter and are packed with the desired catalyst, usually in pellet form. The outside of the reformer shell is covered with a 1/4" thick high temperature insulation under a separate layer of 1" thick Babcock and Wilcox Kaowool. Thermocouples are installed at the top of the shell and in both the heat and process exit pipes. Heat side input is 2" pipe, but output is reduced to 1-1/2" pipe for availability and economics.

The process side directs all the flow from the 1/2" input pipe through three of the stainless steel tubes cored with steel rods to create a 1/16" annulus to promote heat transfer. The three tubes are connected through 3/8" tubing across the top to the three catalyst tubes. The process gas exits through 1" pipe. Modifications to the reformer included thermocouple mounts, pipe size changes, gasket and seal redesign, base construction and a special carbon detector assembly covered later in the instrumentation section of this chapter.

2.3.1.3 Superheater. The superheater makes use of excess reformer heat to insure that the process flow (methanol/water mix) is superheated before it enters the reformer. A spiral coil of 1/2" stainless steel tubing is wound around an 8" diameter steel core with 1" spacing between turns. A steel sheet is wrapped around this and the ends sealed so that the process gas flows through the 1/2" tube in one direction while the excess heat flows in the reverse direction in the spaces between turns in the coil. Excess heat enters and exits through 1-1/2" pipe, while fittings on the tubing allow the

process gas to enter and exit through 1/2" pipe. Thermocouples are mounted at the entrance and exit points for both flows. There are 49 feet of tubing inside the 52" tall superheater, and a 7' angle iron stand is welded to the interior of the core so that the unit can be mounted between the reformer and evaporator with minimum piping and heat loss. The whole unit is wrapped in 1" Kaowool and filled with W.R. Grace Zonolite (vermiculite) inside the hollow core. Changes made to the superheater include tube fittings, mounting stand, insulation and piping between other units.

2.3.1.4 Evaporator. The evaporator uses the lowest grade excess heat from the reformer to do the initial heating of the methanol/water mix from room temperature liquid to a superheated gas. It is made in similar fashion to the superheater but the coils are wound as close together as possible and the excess heat flows in a much smaller space. The evaporator is 27" tall, mounted on a 7' angle iron and placed for minimum heat loss. Input and exit lines for the excess heat are 1-1/2" pipe which increases to 2" before it enters the building exhaust piping. Input line for the process liquid feed is 3/8" copper tubing and the exit line is 1/2" pipe. Thermocouples are mounted at input and exit of each flow. The unit is covered with 1/4" of high temperature insulation and a layer of 1" Kaowool over that. Zonolite fills the hollow center. Modifications to this unit include process line fittings, mounting stand, insulation and straight-flow of the exit heat into the building exhaust.

2.3.1.5 Exhaust System. The AME building exhaust manifold system carries the excess heat through piping of expanding diameter until an 8" pipe vents it to the atmosphere above the building. A shutoff valve between the evaporator and the exhaust system can be closed to protect the reformer units from contamination when other engine lab operations are exhausting into the system.

2.3.2 Process Flow Side

The process flow side of the reformer system begins with a mix of methanol and water at a known ratio and ends either in a sample bottle, or as hydrogen and carbon dioxide burned off and exhausted through a large overhead vent fan.

2.3.2.1 Methanol/Water Source. Laboratory grade methanol is purchased at University Stores in five-gallon quantities, although a partially used fifty-five-gallon drum of the same has been the source so far. Deionized water is obtained through an agreement with the Electrical Engineering Solid State Lab Assistant, Doug Blacke. Methanol and water are mixed in the required ratio and stored in a 4000 ml glass beaker. Additional methanol/water mix is added to the beaker as necessary during the sampling run.

2.3.2.2 Methanol/Water Pump. The pump provides methanol/water mix to the process side at a controlled, but variable, rate. The Fluid Metering, Inc., Model RPP positive displacement pump has its displacement controlled by a micrometer adjustment. An Electro Products Model EFB Variable DC Power Supply provides power to the pump and controls speed. Exact measurements of the flow rate are made by

timing the methanol/water level through a known drop in a glass tube and converting centimeters of drop per second to milliliters of flow per second (1 cm = 3.82 ml). See Figure 18.

2.3.2.3 Evaporator and Superheater. The methanol/water mix flows through the stainless steel tubing in these previously described units, normally exiting the evaporator at a temperature above boiling, and exiting the superheater well into the superheated range. Temperature and pressure measurements are made between units.

2.3.2.4 Reformer. The methanol/water mix (now completely vaporized) enters the process stream tubes of the reformer, picks up additional heat, and then begins to flow down through the three catalyst-bearing tubes. Previously the AME reformer had been loaded with Girdler G-59 catalyst in 1/4" pellets (Scott 1979, p. 9). Others reported using Girdler G-9 and G-66B (Kester and others 1975c, p. 10). Dr. Kerwin provided us with a new catalyst which LASL was interested in, and the reformer was loaded with 3,058 grams (14,646 3/16" pellets with catalytic surface of 16.85 square feet and a volume of 1,242.64 cubic centimeters) (Bertrand 1979). The catalyst was assumed similar to Girdler's G-66B copper-zinc type, but it is known only as LASL Number T-2130 (German). It had a distinctively different greenish tint when compared to the previously loaded catalyst which was grayish. The catalyst was activated initially by running nitrogen for 20 minutes then hydrogen for 30 minutes at 2 psig and at reformer heat side output temperature of more than 500°F. The process gas exits the reformer in 1" pipe and its temperature and pressure are measured.

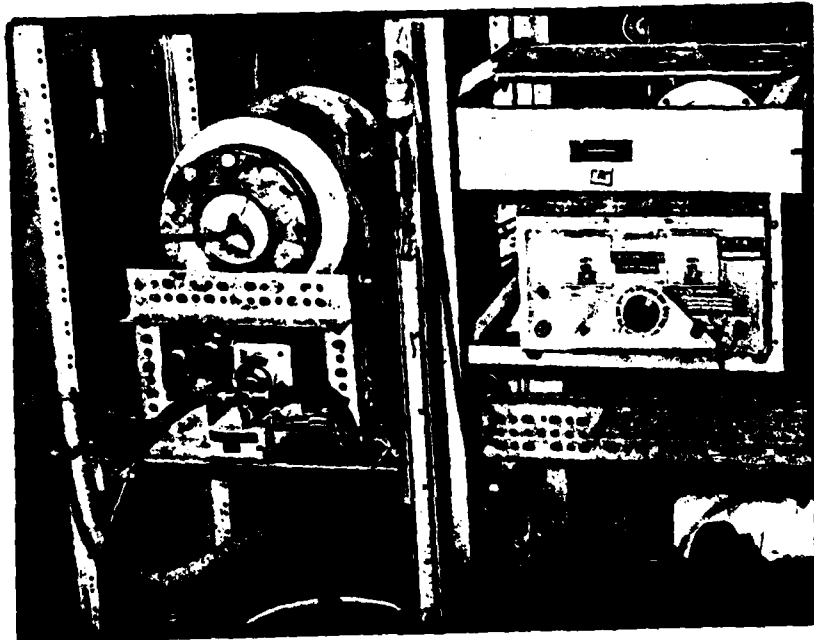


Figure 18. Process Pump and Controls

2.3.2.5 Condenser. The condenser is designed to cool the superheated process gas and condense water and unreacted methanol for sampling as liquids. The 1" pipe flows into a condenser coil manifold of three 3/4" finned tubes set in a water bath tank 23" in diameter with an open top and steady flow of cooling water. This cooled the process stream to 75-85°F but some liquid still condensed at points downstream in the lines. A refrigerated water chiller was added to reduce the cooling water temperature further and prevent the late condensation.

2.3.2.6 Separator. Process vapor and liquid from the condenser tangentially enter a 2" diameter 24" long separator pipe which allows the vapor to rise and flow onward while dropping the liquid condensate into a 2-1/2 gallon receiver tank (see Figure 19).

2.3.2.7 Sampling. Sampling is accomplished at both ends of the separator. Liquid condensate is removed for the period of interest by opening the valve at the bottom of the receiver tank. The total amount is measured, the specific gravity is checked and a small bottle is sent to the University Analysis Lab (2nd Floor, Biology Building, Mr. Jarvis Moyers, Director) for methanol content analysis. Process gas sampling is done just above the separator by special valving which allows evacuation of the sample bottle to eliminate impurities in the lines. The valving is then reset to allow process stream pressure to fill the sample bottle at 5-10 psig. The process stream outlet valve can be adjusted to control sample bottle pressure. A specially constructed valve mated to the sample bottle is then

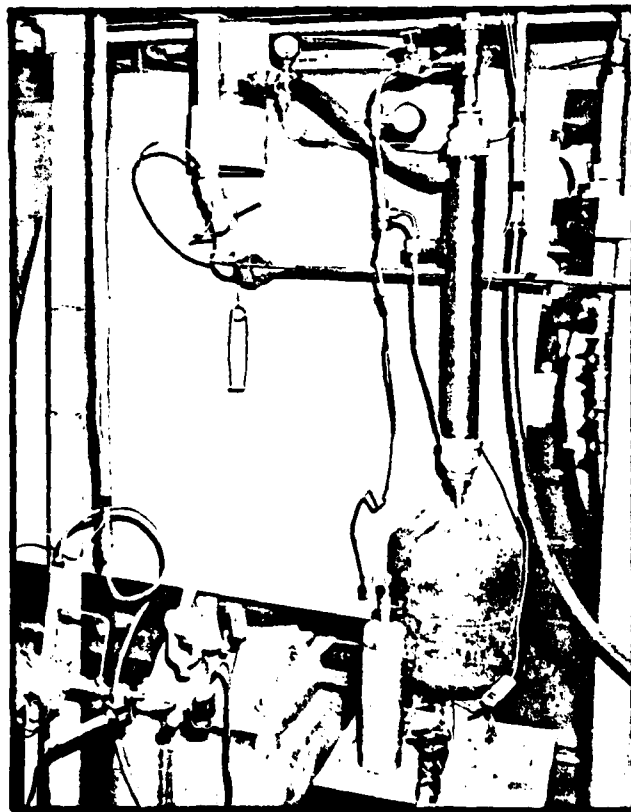


Figure 19. Process Separator and Burner

closed, the bottle removed, and another installed if further sampling is necessary. The sample bottles are extensively reworked propane cylinders which provide enough sample volume for the analysis lab to analyze. The lab checks the sample for volume % of hydrogen, carbon dioxide, carbon monoxide and methane. This requires that the AME Department furnish the lab with certified standard mixes of these four gases in ratios close to the expected results so that their chromatograph equipment can be calibrated. Current sample analysis takes a week or more, and Jim Blair has taken on a Master's Project of installing a gas chromatograph in-line with the system so results can be immediately known. The capabilities of this system will be nearly unlimited once that is completed.

2.3.2.8 Flowmeter. The process gas not taken for sampling is routed through a Fisher Porter flowmeter to give a backup check on amount of methanol converted.

2.3.2.9 Process Burner. Many hours were spent considering what safety precautions to take with the process gas stream. Although the composition was not known, we hoped that hydrogen would be the dominant constituent, and if so, it had to be disposed of safely. Re-use in the Willan/Reid burner was discussed but not favored because it introduced a very large unknown factor into Susan Hyde's thermodynamic studies, and a flameout might put unsafe amounts of hydrogen into the system and building exhaust piping. The safest choice appeared to be burning the excess process gas, and a burner tube, with natural gas pilot light, was designed and installed in the center of

the vent hood. The large volume of airflow with the hood vent fan on necessitated adding a special nozzle and baffle to keep the pilot light flame lit. The upper left of Figure 19 and the drawing in Figure 20 show the current design. The burned gas is then exhausted through the vent hood and out of the building.

2.3.3 Instrumentation and Control

Since the overall system occupies a space approximately 10 feet by 6 feet, the instrumentation problem was primarily one of centralization of data monitoring and process control. However, because of the varied requirements for data (temperature, pressure, flow) and control (water, air, gasoline, natural gas, electric) and the size of the system (Figure 21) all instrumentation and control elements could not be placed on one panel. To evaluate the variables listed at the beginning of this chapter (temperature, pressure, flow-rate, catalyst and methanol/water ratio) we installed thermocouples, pressure gauges, a computer data system, flowmeters, a carbon detector system and a central control panel.

2.3.3.1 Thermocouples. Thermocouples were placed at strategic points on the system to provide necessary temperature information. The old systems had also used thermocouples but had left no record of what type they were, what calibration they had or which ones still worked. We determined that most of the available thermocouples were Chromel/Alumel manufactured by Omega Engineering, Incorporated. Omega listed their Chromel/Alumel thermocouples as type K, useful from -300°F to 2300°F with an output range of -5.51 to 51.05 millivolts (Omega

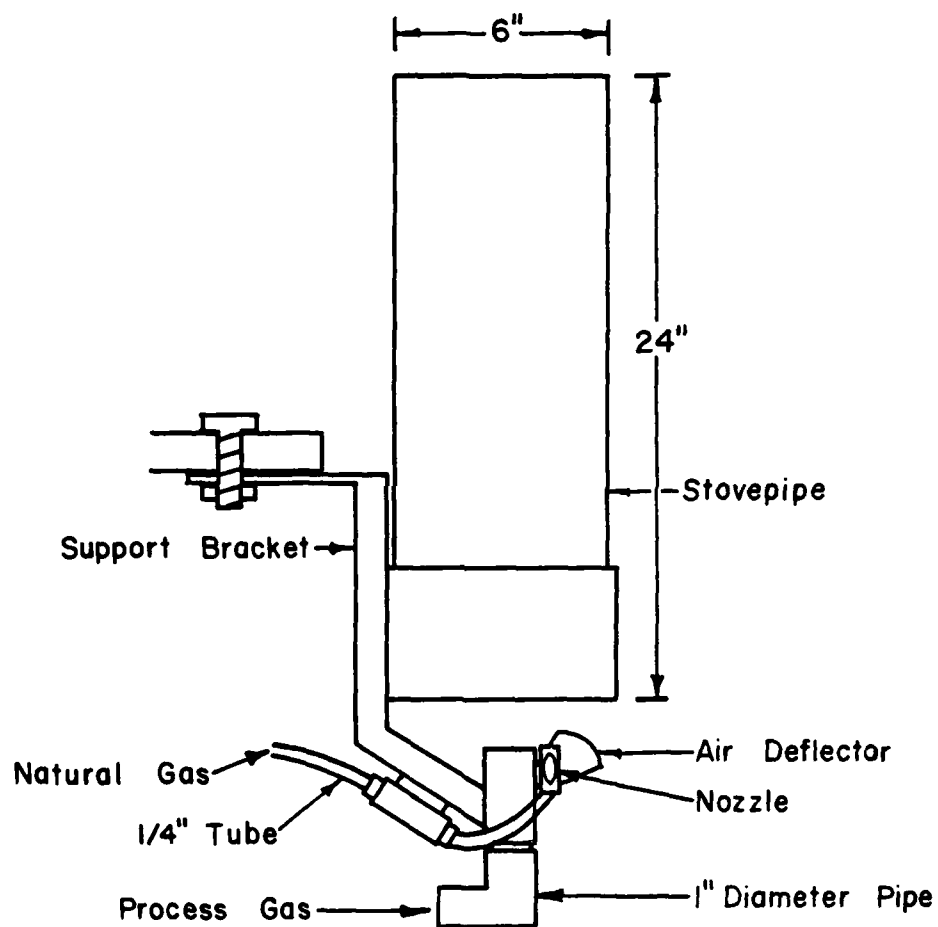


Figure 20. Process Gas Burner

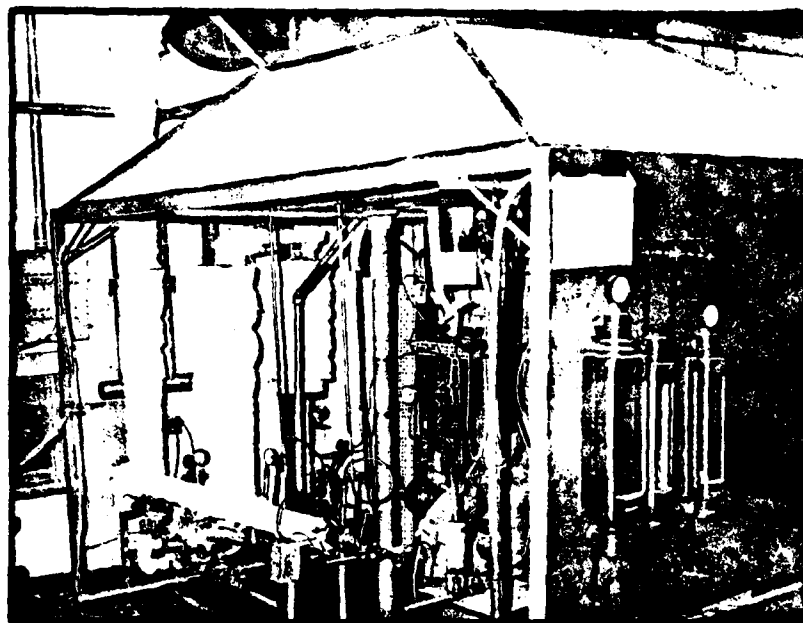


Figure 21. Overall System Installation

1972, p. A-2). Although the old data system required an elaborate amplifier setup to interface with these output levels, the newly purchased Hewlett Packard (HP) 3052A System would take direct input at this millivolt range. Since the temperature range was also what was required, we decided to use these thermocouples and located a few more around the AME Department. The outputs were checked against Table 10 values in both low temperature hot water and a high temperature oven. Output millivolt measurement was made with an HP 3465A Digital Multimeter and crosschecked on the HP System 3052A voltmeters when they arrived. The readout pyrometer, Newport Model 267 Digital Pyrometer, was also checked against these known outputs and registered within 5%, which is the design tolerance of the instrument (see Table 11). When all thermocouples had been checked for correct operation and calibration, they were placed on the system at the points listed in Table 12. Since the millivolt outputs from the thermocouples had to be transmitted two floors up, the existing shielded cable system was checked for losses and rewired to use up to 16 channels. The #18 standard, two conductor foil shielded cable with drain wire carried the signals with virtually no loss. A Department-wide standard plug was adopted for the HP 3052A System and the thermocouple inputs were wired to that plug in order to match the interface requirements of the HP 3495A scanner (see Table 13). Howard Silverman wrote the HGO program for the HP 9835 computer which uses an 8th order curve-matching equation to transform the millivolt inputs into temperature outputs in $^{\circ}\text{F}$ and $^{\circ}\text{C}$ (see Appendix A). The Newport pyrometer temperature

Table 10. Thermocouple Conversion Table

DEG C	0	1	2	3	4	5	6	7	8	9	10	DEG C
THERMOELECTRIC VOLTAGE IN ABSOLUTE MILLIVOLTS												
0	0.000	0.009	0.019	0.029	0.039	0.049	0.059	0.069	0.079	0.089	0.099	0
10	0.397	0.437	0.477	0.517	0.557	0.597	0.637	0.677	0.717	0.757	0.797	10
20	0.798	0.838	0.879	0.919	0.960	1.000	1.041	1.081	1.122	1.162	1.203	20
30	1.203	1.244	1.285	1.325	1.366	1.407	1.448	1.489	1.529	1.570	1.611	30
40	1.611	1.652	1.693	1.734	1.774	1.817	1.858	1.899	1.940	1.981	2.022	40
50	2.022	2.064	2.105	2.146	2.188	2.229	2.270	2.312	2.353	2.394	2.436	50
60	2.436	2.477	2.519	2.560	2.601	2.643	2.684	2.726	2.767	2.809	2.850	60
70	2.850	2.892	2.933	2.975	3.016	3.058	3.100	3.141	3.183	3.224	3.266	70
80	3.266	3.307	3.349	3.390	3.432	3.473	3.515	3.556	3.598	3.639	3.681	80
90	3.681	3.722	3.764	3.805	3.847	3.888	3.930	3.971	4.012	4.054	4.095	90
100	4.095	4.137	4.178	4.219	4.261	4.302	4.343	4.384	4.426	4.467	4.508	100
110	4.508	4.549	4.590	4.632	4.673	4.714	4.755	4.796	4.837	4.878	4.919	110
120	4.919	4.960	5.001	5.042	5.083	5.124	5.164	5.205	5.246	5.287	5.327	120
130	5.327	5.368	5.409	5.450	5.490	5.531	5.571	5.612	5.652	5.693	5.733	130
140	5.733	5.774	5.814	5.855	5.895	5.936	5.976	6.016	6.057	6.097	6.137	140
150	6.137	6.177	6.218	6.258	6.298	6.338	6.378	6.419	6.459	6.499	6.539	150
160	6.539	6.579	6.619	6.659	6.699	6.739	6.779	6.819	6.859	6.899	6.939	160
170	6.939	6.979	7.019	7.059	7.099	7.139	7.179	7.219	7.259	7.299	7.338	170
180	7.338	7.378	7.418	7.458	7.498	7.538	7.578	7.618	7.658	7.697	7.737	180
190	7.737	7.777	7.817	7.857	7.897	7.937	7.977	8.017	8.057	8.097	8.137	190
200	8.137	8.177	8.216	8.256	8.296	8.336	8.376	8.416	8.456	8.497	8.537	200
210	8.537	8.577	8.617	8.657	8.697	8.737	8.777	8.817	8.857	8.898	8.938	210
220	8.938	8.978	9.018	9.058	9.099	9.139	9.179	9.220	9.260	9.300	9.341	220
230	9.341	9.381	9.421	9.462	9.502	9.543	9.583	9.624	9.664	9.705	9.745	230
240	9.745	9.785	9.826	9.867	9.907	9.948	9.989	10.029	10.070	10.111	10.151	240
250	10.151	10.192	10.233	10.274	10.315	10.355	10.396	10.437	10.478	10.519	10.560	250
260	10.560	10.600	10.641	10.682	10.723	10.764	10.805	10.846	10.887	10.928	10.969	260
270	10.969	11.010	11.051	11.093	11.134	11.175	11.216	11.257	11.298	11.339	11.381	270
280	11.381	11.422	11.463	11.504	11.546	11.587	11.628	11.669	11.711	11.752	11.793	280
290	11.793	11.835	11.876	11.918	11.959	12.000	12.042	12.083	12.125	12.166	12.207	290
300	12.207	12.249	12.290	12.332	12.373	12.415	12.456	12.498	12.539	12.581	12.623	300
310	12.623	12.664	12.706	12.747	12.789	12.831	12.872	12.914	12.955	12.997	13.039	310
320	13.039	13.080	13.122	13.164	13.205	13.247	13.289	13.331	13.372	13.414	13.456	320
330	13.456	13.497	13.539	13.581	13.623	13.664	13.706	13.748	13.790	13.832	13.874	330
340	13.874	13.915	13.957	13.999	14.041	14.083	14.125	14.167	14.208	14.250	14.292	340
350	14.292	14.334	14.376	14.418	14.460	14.502	14.544	14.586	14.628	14.670	14.712	350
360	14.712	14.754	14.796	14.838	14.880	14.922	14.964	15.006	15.048	15.090	15.132	360
370	15.132	15.174	15.216	15.258	15.300	15.342	15.384	15.426	15.468	15.510	15.552	370
380	15.552	15.594	15.636	15.678	15.721	15.763	15.805	15.847	15.889	15.931	15.973	380
390	15.973	16.015	16.058	16.100	16.142	16.184	16.227	16.269	16.311	16.353	16.395	390
400	16.395	16.438	16.480	16.522	16.564	16.607	16.649	16.691	16.733	16.775	16.818	400
410	16.818	16.860	16.902	16.945	16.987	17.029	17.072	17.114	17.156	17.199	17.241	410
420	17.241	17.283	17.326	17.368	17.410	17.453	17.495	17.537	17.580	17.622	17.664	420
430	17.664	17.707	17.749	17.792	17.834	17.876	17.919	17.961	18.004	18.046	18.088	430
440	18.088	18.131	18.173	18.216	18.258	18.301	18.343	18.385	18.428	18.470	18.513	440
450	18.513	18.555	18.598	18.640	18.683	18.725	18.768	18.810	18.853	18.895	18.938	450
460	18.938	18.980	19.023	19.065	19.108	19.150	19.193	19.235	19.278	19.320	19.363	460
470	19.363	19.405	19.448	19.490	19.533	19.576	19.618	19.661	19.703	19.746	19.788	470
480	19.788	19.831	19.873	19.916	19.959	20.001	20.044	20.086	20.129	20.172	20.214	480
490	20.214	20.257	20.299	20.342	20.385	20.427	20.470	20.512	20.555	20.598	20.640	490
500	20.640	20.683	20.725	20.768	20.811	20.853	20.896	20.938	20.981	21.024	21.066	500
510	21.066	21.109	21.152	21.194	21.237	21.280	21.322	21.365	21.407	21.450	21.493	510
520	21.493	21.535	21.578	21.621	21.663	21.706	21.749	21.791	21.834	21.876	21.919	520
530	21.919	21.962	22.004	22.047	22.090	22.132	22.175	22.218	22.260	22.303	22.346	530
540	22.346	22.388	22.431	22.473	22.516	22.559	22.601	22.644	22.687	22.729	22.772	540
550	22.772	22.815	22.857	22.900	22.942	22.985	23.028	23.070	23.113	23.156	23.198	550
560	23.198	23.241	23.284	23.326	23.369	23.411	23.454	23.497	23.539	23.582	23.624	560
570	23.624	23.667	23.710	23.752	23.795	23.837	23.880	23.923	23.965	24.008	24.050	570
580	24.050	24.093	24.136	24.178	24.221	24.263	24.306	24.348	24.391	24.434	24.476	580
590	24.476	24.519	24.561	24.604	24.646	24.689	24.731	24.774	24.817	24.859	24.902	590
600	24.902	24.944	24.987	25.029	25.072	25.114	25.157	25.199	25.242	25.284	25.327	600
DEG C	0	1	2	3	4	5	6	7	8	9	10	DEG C

Source: Omega, 1972, p. A-2.

Table 11. Thermocouple and Pyrometer Check

Water Temp. ($^{\circ}\text{F}$)	Reference Junction ($^{\circ}\text{F}$)	Temp. Readout ($^{\circ}\text{F}$)	mv Total	mv from Omega Chart	mv Error
90	84	89	1.29	1.294	-.004
100	84	100	1.52	1.520	0
110	83	113	1.74	1.748	-.008
120	83	124	1.97	1.977	-.007
130	83	135	2.20	2.206	-.006
140	83	146	2.43	2.436	-.006
150	83	156	2.66	2.666	-.006
160	83	169	2.89	2.896	-.006
170	83	179	3.12	3.127	-.007
180	83	191	3.36	3.358	+.002
190	84	202	3.59	3.589	+.001
200	84	212	3.82	3.819	+.001

Table 12. Thermocouple Locations

TC #	Location	Expected Temp (^o F)
1	Willan/Reid Burner Output	1000-1300
2	Reformer Process Output	500-1000
3	Reformer Heat Output	500-1000
4	Superheater Process Output	400- 800
5	Evaporator Process Output	200- 600
6	Superheater Heat Output	500-1000
7	Evaporator Heat Output	200- 500
8	Evaporator Process Input	80- 100
9	Condenser Process Output	80- 150
10	Separator Process Liquid Output	80- 150
11	Separator Process Gas Output	80- 150
12	Willan/Reid Burner Primary Air	100- 500
13	Reformer Heat (Top)	500-1200
14	Reference Junctions	70- 100

Table 13. Thermocouple/Data System Interface

TC Number	Scanner Channel	Plug Number
1	00	1
2	01	1
3	02	1
4	03	1
6	04	1
8	05	1
12	06	1
13	07	1
5	08	1
7	09	1
9	10	2
10	11	2
11	12	2
14	13	2

readout was internally compensated, but the HP system voltmeters were not. Therefore, because thermocouple output voltages are based on one hot junction and one cold junction, referenced to 0°C (32°F), the thermocouple wiring became a small problem because of the requirement to use both the readout (for immediate in-lab checks) and the HP computer (for later thermodynamic analysis). In Figure 22, "A" depicts the wiring required by the in-lab readout, "B" shows the wiring required by the HP computer, and "C" shows the final design which permits both to operate without error. Before deciding on "C" numerous other designs were tested but the resulting errors ranged from 10% to 20%. The cold junction shown in parts "B" and "C" of Figure 22 is wired inside the main control panel; it is not at 0°C (32°F). This error is compensated however, with the installation of an Omega Engineering Electronic Icepoint (Figure 23) (Omega 1977, p. 6) in line with thermocouple #14 which transmits the reference junction temperature to the computer. The HGO program then adds the output of any thermocouple to the voltage output from the compensated cold junction to obtain the actual voltage it must convert to temperature. A 20 position rotary switch allows selection of any thermocouple at the in-lab control panel, and the HP 3495A scanner continuously checks all thermocouples for the computer.

2.3.3.2 Pressure Measurement. Although our plans called for very low pressure (near atmospheric) applications, some pressure measurement system was still required. Original plans called for installation of the AME Department's National Semiconductor pressure

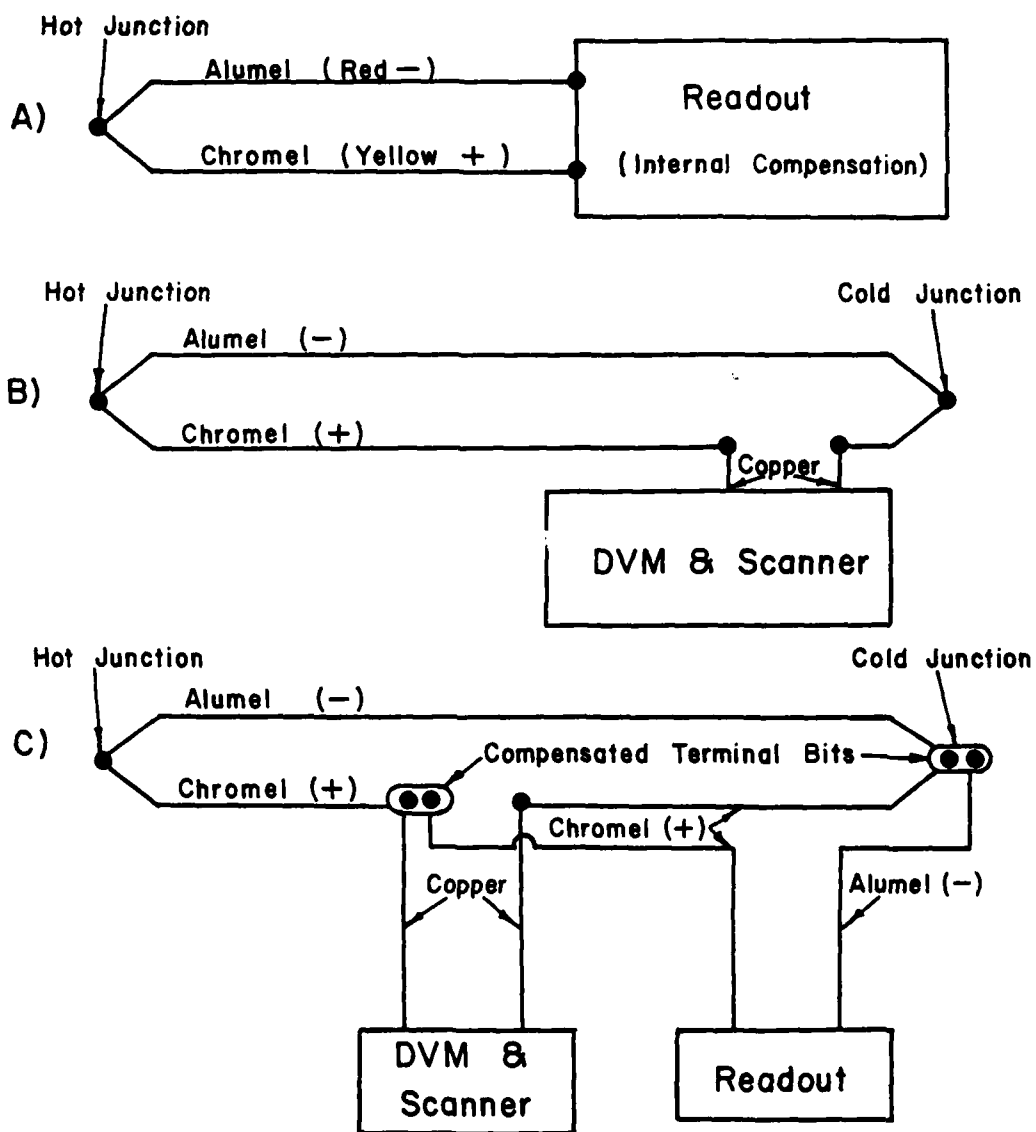
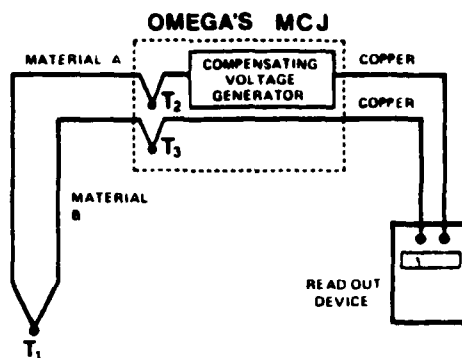


Figure 22. Thermocouple Wiring



SPECIFICATIONS

Fixed Reference Temp. Setting

0°C (32°F) standard

* Compensation Accuracy

$\pm 1/2^\circ\text{C}$ from 15°C (59°F)
to 30°C (86°F) ambient

$\pm 1^\circ\text{C}$ from 10°C (50°F)
to 45°C (113°F) ambient

Impedance

Less than 200 ohms

*for standard reference temperature setting

Figure 23. Omega Icepoint Specifications
-- Source: Omega 1977, p. 6.

transducers. However, at a cost well above \$100.00 each and considering our need for 12 of them, the Department Head suggested that we mount them on a portable stand with a system of overpressure protection valves. Estimates of the time and cost to construct this portable mounting convinced us to build the reformer system with simple pressure gauges which might later be replaced or complimented by the transducers. Standard gauges were mounted at the same points where thermocouples were installed (see Table 12) except at the top of the reformer. All gauges on the process stream side had a maximum range of 30 psig, while those on the heat side ranged up to 160 psig. Additional gauges were placed on the gasoline tank compressed air regulator (0-15 psig), the main air flow meter for the Willan/Reid burner, and the process gas output flowmeter. These were read and recorded by hand, as necessary, during a run. The heat side is normally at 0 psig, and the highest pressure on the process side is between the pump and evaporator at up to 15 psig.

2.3.3.3 Data System. The data system chosen had to give immediate information for in-lab correction, and store information for later analysis. In-lab data was recorded by hand as necessary from the Newport Pyrometer temperature readout, flowmeters and pressure gauges. The data storage system for later analysis was the Department's new HP 3052A System which included a 9835A computer with CRT, a 3455A digital voltmeter, a 3437A system voltmeter, a 3495A scanner and a 9872A plotter. Both the in-lab and HP computer systems were

much more accurate, reliable and useable than the past Digital DEC 10 system with amplifiers.

2.3.3.4 Flowmeters. These Fisher Porter meters were installed on the air lines into the Willan/Reid burner and the process gas output line to measure flow as a % of full-scale capability. They were all mounted on a single flowmeter panel with necessary valves to control the flow through them. The data they provided was used for in-lab burner adjustment or as backup information on hydrogen production.

2.3.3.5 Carbon Detector. Previous reformer projects have had problems with carbon formation when the amount of water in the methanol/water mix was too low or when lower grade methanol was used (Kester and others 1975a, p. 4) and their recommendations were that experimental programs be conducted to aid in understanding and preventing carbon deposition on the catalyst. Later studies showed that a methanol/water ratio of 1:1.3 would prevent carbon buildup, but a reduction of that ratio toward 1:1 would reduce the weight penalty of carrying water. Also, initial work on either ethanol or lower grade methanol has yet to be done, and carbon deposition studies will be an important part of that research. Therefore, we designed a simple carbon detector based on the premise that surface resistance of the catalyst would be reduced by carbon buildup. Figure 24 shows a schematic of our design which consisted of a stainless steel welding rod, 1/16" diameter, inserted through the bottom reformer wall and imbedded approximately 18" into one catalyst bearing tube. The use of Sauereisen Electric Resistor Cement between the rod and the copper

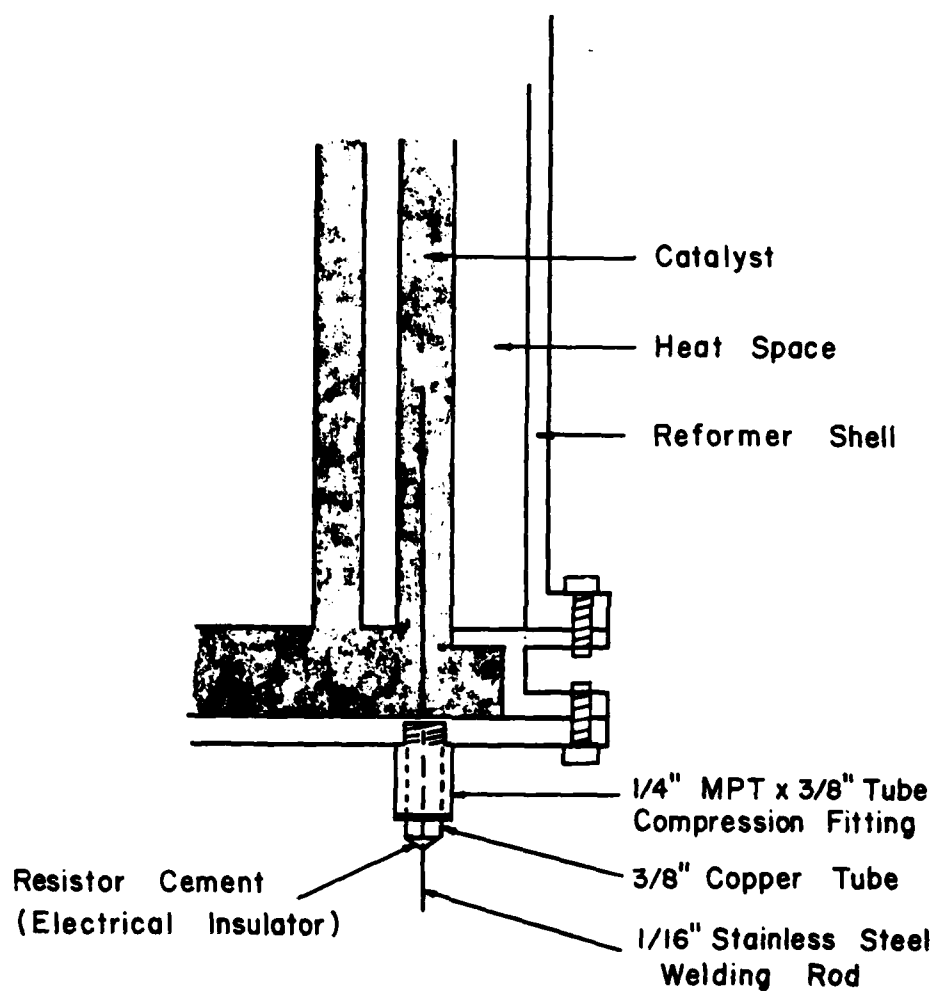


Figure 24. Carbon Detector

tube gave a secure, leak-proof mount, yet electrically insulated the rod from the reformer shell. The cement resists acids, oils and temperatures up to 3000°F, and was chosen after our tests with Litharge and Glycerin (a mix of powdered red lead oxide, Pb_3O_4 , and white lab grade glycerin, $(\text{C}_3\text{H}_8\text{O}_3)$) failed to produce a strong bond despite varied mix ratios, added heat and long drying time. The rod was originally hand packed in the catalyst bed as the catalyst pellets were added so it would not touch the tube and create an electrical short. Initial resistance measurement with the reformer in place using an HP 3465A digital Multimeter showed 1.9 M Ω between the rod and the reformer shell, so it appeared to be a very good starting point. However, with each application of high temperature, even without a process gas flow, the carbon detector resistance became lower and after high temperatures were removed, it rebounded to a lower level. For example, after complete cooling from the first shakedown run, which was done with pure water, the resistance measured 600 Ω , down from 1.9 M Ω . After the second run it was 530 Ω ; after the next run it was 404 Ω ; then 277 Ω ; and after complete cooling from the November 8 run it measured 230 Ω . It appears that the repeated applications of high temperature are bringing the resistance to an equilibrium point where the resistance at the beginning of a run will equal the resistance after cooling. When a few more runs establish that point, a graph of behavior with temperature can be drawn and deviations (lower resistance) from that curve should indicate carbon deposition. The only method currently available to measure carbon deposition is to

unload the catalyst and have it analyzed. We have run checks at the completion of a methanol/water process run, in which only water is pumped through. Once the process gas stream flame burns out, any gas being formed would be a carbon and oxygen combination formed by removing carbon from the catalyst. The flowmeter indicated zero flow at the same time the process flow failed to support a flame so no gas of any type was being produced. Thus, the catalyst was still very clean. The % conversion of methanol also confirmed a clean catalyst, so effective use of the carbon detector must wait until the effects of high temperature applications have settled into an equilibrium condition.

2.3.3.6 Control Panel. The in-lab control panel contains centralized control switches for as much equipment as could be logically combined there. Figure 25 pictures the portable cabinet which contains, from top to bottom: the multimeter carbon detector resistance readout; a spare power supply; the Newport pyrometer temperature readout; the Omega 20 channel switch that selects a thermocouple for readout on the pyrometer; SPST power switches for the igniter, fuel solenoid, vacuum pump, west side outlet (methanol/water pump and condenser water chiller), and pyrometer; and the igniter power supply. This unit is portable but input/output cable bundles restrict its movement.

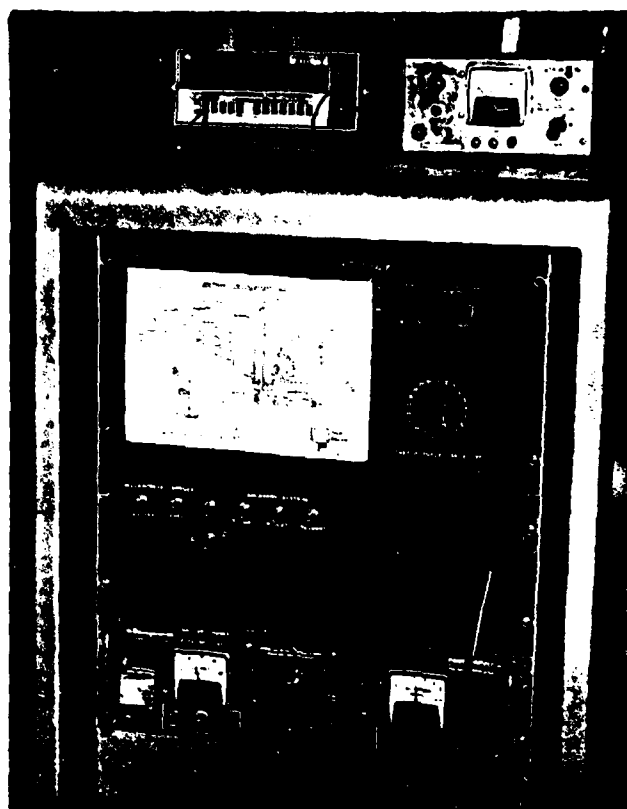


Figure 25. Control Panel

2.4 System Location

The reformer system is a semi-permanent installation in the Aeronautical Engineering Building, Engine Lab, Room 105, on The University of Arizona campus, Tucson, Arizona.

CHAPTER 3

SYSTEM OPERATION

After five months of design and construction work, the system was ready for its first run in early October 1979. This chapter discusses the shakedown runs and development of standard procedures for safe operation.

3.1 Shakedown Runs

First operation of the system was scheduled for October 9, 1979, as an initial shakedown run, with follow-up tests to be made as necessary. The first two hours of the October 18th run were also used to ready the system; then the first production run began. This section details the problems which arose, and our solutions to them.

3.1.1 Leak Checks

The heat side of the system was pressure checked to 30 psig, although operation as close to 0 psig as possible was anticipated. Air leaks were found in the threads mating the Willan/Reid burner to the reformer and in the reformer shell gasket. The burner tube was removed, the threads filed and a copper-based gasket spray applied. The reformer shell was unbolted, raised and the gasket was coated with Permatex. Both systems were reinstalled and worked correctly.

3.1.2 Willan/Reid Burner Nozzle

This fuel spray nozzle continually clogged because the original filter screen had broken. A new fuel oil burner nozzle was purchased as a backup but the original worked fine after a glass bowl fuel filter was installed. Periodic cleaning for carbon deposition is still required every 10 hours of operation, however. The cleaning job was difficult because a copper gasket on the burner needed precise alignment as 6 bolts required near-simultaneous tightening. A redesigned gasket greatly shortened the time required here.

3.1.3 Temperature Fluctuations

Variations in the air pressure and gasoline fuel pressure created temperature fluctuations at the Willan/Reid burner output as large as $\pm 50^{\circ}\text{F}$. Although this large fluctuation was not immediately reflected in the reformer and other units because of temperature inertia in their structure, it did cause a problem in determining what temperature heat was being added. A new regulator on the fuel pressure line with 0-15 psig gauge for precise control, and a regulator and surgetank dryer on the air pressure side brought the output temperature fluctuations down to $\pm 15^{\circ}\text{F}$. The dryer also eliminated temperature surges caused by water in the air compressor lines, which run throughout the building.

3.1.4 Heat Losses

Past systems had had extensive heat loss problems because of insufficient insulation. Although the reformer, superheater,

evaporator, Willan/Reid burner and all interconnections had been covered with 1" thick Kaowool from Babcock and Wilcox, heat loss was still a problem on the evaporator and superheater because of their unique construction. Their hollow cores served as chimneys and a large-volume airflow through them resulted in critical convection heat loss. The solution was to plug the bottom of the core with what remained of the Kaowool (too expensive to buy more) and then fill the core with vermiculite.

3.1.5 Warmup Time

The first runs indicated we faced a startup time of nearly 2-1/2 hours before the evaporator was hot enough to begin pumping methanol. This was without the vermiculite mentioned above, and at an air flow rate into the burner of about 110 pounds per hour. After the vermiculite was added and optimum airflow and fuel pressure established, startup time was reduced to just under 1 hour.

3.1.6 Gasoline Tank Capacity

The gasoline tank was described in earlier reports as having a 2-1/2 gallon capacity, and it did. However, if the fuel level in the tank exceeded the height of the air pressure inlet fitting, the gasoline crept uphill through the pressure line and filled the pressure regulator. That created uncontrollable fuel pressure and would have ruined the regulator diaphragm. The tank is now limited to about 1-1/2 gallons (until the air line is remounted) which allows

just over 3 hours operation before the tank must be refilled, and current runs do not take that long.

3.1.7 Sample Analysis

This area was not anticipated as a problem. The University Analysis Lab had done the work on a few earlier samples and agreement had been reached with the Lab Director to provide analysis for an unspecified interdepartmental funding fee. However, the lab has a workload which only allows it to process one gas sample of ours per week. This effectively limits our testing to once a week, because the previous results must be known to proceed intelligently. In addition, after receiving the first two samples the lab found it had no more certified standard gas mixtures comparable to our expected product, and they could not calibrate their analysis equipment to give us quality results. Liquid condensate samples can be analyzed without the known gas mixtures, but they do little good without the gas results. Therefore, the reformer test runs were limited to one a week from October 25 on, and results were stopped after two samples until the certified gas mixtures of hydrogen, carbon dioxide, carbon monoxide and methane arrive. As a solution to this problem, Jim Blair has undertaken as his Master's Project the on-line operation of a gas chromatograph which the AME Department already owns. This modification will give reformer operators the capability to make immediate changes in any of the variables during any test run rather than waiting for lab analysis.

3.2 Standard Procedures for Safety

Because of the explosive nature of hydrogen if incorrectly managed, specific procedures were developed to allow safe operation of the system. These checklists for Startup, Sampling and Shutdown are found in Appendix B of this paper.

CHAPTER 4

RESULTS

Although sample analysis has limited operation so far, enough data has been gathered to predict results, compare actual results with those predictions, and to compare results with the requirements for fuel cell operation.

4.1 Predicted Results

Louis Bertrand's predicted results in Figure 12 were based on equilibrium conditions without knowledge of specific reformer system kinetics. Beginning with calculations for methanol/water ratios (Table 14) and using data gathered on the early runs (Table 15), Susan Hyde wrote a computer program (Hyde 1979) to predict process gas makeup for given ratios and catalyst bed temperature. Further thermodynamic analysis will be available in her Master's Report on the subject, but an example of the predicted makeup for a methanol/-water ratio of 1:1.3 is found in Table 16. Figures 7-11 also give general indications of expected output, though any specific reformer system will differ somewhat. Catalyst differences must also be taken into account when comparing Figures 7-11 to Table 16.

Table 14. Calculations for Methanol/Water Ratios

$\text{CH}_3\text{OH}/\text{H}_2\text{O}$ Mole Ratio	ml $\text{H}_2\text{O}/$ 1 CH_3OH	% CH_3OH By Weight	Solution Grams/l	Moles CH_3OH Per Liter Solution
1:1.0	447.6	64.01	888.9	.03915
1:1.1	492.4	61.78	893.9	.03800
1:1.2	537.1	59.71	898.4	.03691
1:1.3	581.9	57.77	902.6	.03588
1:1.4	626.6	55.96	906.4	.03490
1:1.5	671.4	54.25	909.9	.03396

Table 15. Steady State Temperature Profile -- Table 12 for TC location.

Run No.	<u>°F, Heat Side, TC Number:</u>				<u>°F, Process Side, TC Number:</u>				
	1	3	6	7	8	5	4	2	9
Trial 1	1170	725	415	195	100	250	556	462	102
Trial 2	1114	586	377	230	89	187	297	326	89
2	1160	639	504	169	88	515	631	663	102
3	790	462	336	185	77	290	386	384	85
4	640	407	310	132	70	197	375	388	88
5	477	425	347	143	78	206	407	419	93

Table 16. Predicted Product Makeup -- Volume %, dry, 1:1.3 ratio, atmospheric pressure.

Temperature		H ₂	CO ₂	CO
°K	°F			
300	81	75%	25%	0%
400	261	75	25	0
500	441	74.9	24.6	0.5
600	621	74.4	23.2	2.4

4.2 Actual Results

Table 17 lists actual product gas makeup on a dry basis (water removed). All results are from a methanol/water ratio of 1:1.3.

4.2.1 Comparison of Results with Predictions

The sample from the first test run was lost because when the sample bottle cooled, the contents went below atmospheric pressure and the lab could not analyze it.

The subsequent runs show a quite good relationship between Tables 16 and 17, indicating that not only can methanol be reformed at temperatures below 400°F, but also that once specifics of reformer design are known, predictions of the reformed product can be more accurate.

4.2.2 Comparison of Results with Fuel Cell Requirements

As noted in Chapter 1, the fuel cell under consideration requires a hydrogen-rich carbon monoxide-poor input stream. If the fuel cell is to provide the heat to reform methanol into this fuel stream, methanol must be reformable at or below about 400°F (204°C). Finally, if the reformer system is to work in a vehicle application, a size small enough for that must also provide enough hydrogen to power the fuel cell.

Examination of Table 17 demonstrates that reformation of a methanol/water mix can provide the necessary hydrogen-rich carbon monoxide-poor fuel stream; it also demonstrates that such a fuel stream can be produced at temperatures low enough that only waste

Table 17. Product Makeup

Run No.	TC #2 °F	Dry Gas Sample				% Conversion of CH ₃ OH
		% H ₂	% CO ₂	% CO	% CH ₄	
Trial 1	---	---	---	---	---	None
Trial 2	---	---	---	---	---	None
2	663	65.0	25.0	<1.0	1.0	85.5
3	384	---	---	---	---	---
4	388	74.0	25.0	0.1	<0.1	80.1
5	419	75.0	27.0	0.2	<0.1	77.0

heat in liquid form from the fuel cell is required to reform the methanol. Finally, the reformer we used had catalyst material in three tubes, each 1" diameter and 7' long. Judging from other designs, that could also be designed as twenty-one tubes, 1" diameter and 1' long; which could easily be placed in a form about 1' high, 1/2' wide and 1-1/2' long. Such a form could conveniently fit in a small size car, sharing the engine compartment with the fuel cell components now under consideration at LASL. The remaining question, however, is what amount of hydrogen, rather than %, is required and produced. Early LASL testing on the golf cart mounted fuel cell required 49 liters of hydrogen per minute during maximum output bursts. The reformer run of November 8 produced a steady flow of 0.32 pound-mole of product gas per hour (Bertrand 1979, p. 6). Using conversion factors of 386 cubic feet per pound-mole under standard conditions and 28.32 liters per cubic foot, the product gas was produced at a rate of 58.34 liters per minute. Thus, if hydrogen were 83.9% of the product, it would produce exactly the amount needed by the fuel cell at maximum power. The normal hydrogen volume % (dry) is between 60 and 75%, however (Tables 16 and 17) so either a greater methanol/water flow rate or a larger catalyst volume would be required. The November 8 run had methanol/water input rate of 5.81 liters per hour (0.208 pound-moles per hour) when it produced 4.02 pounds per hour (0.32 pound-moles per hour) of product gas. A vehicle fuel consumption rate of even double the 5.81 liters per hour at maximum performance would not be bad, especially considering nearly 40% of that fuel is water!

For additional results recorded after completion of this paper, see Louis Bertrand's extensive notebooks of chemical analysis (1979). The final two test runs shown in Table 17 are the most reliable because the lab was given a certified standard mix of gases similar to our expected product. This mix allowed them to purge and calibrated their chromatograph.

CHAPTER 5

CONCLUSIONS

5.1 Reliable System

The University of Arizona now has an operating, reliable reformer system, capable of "universal" application to goals of at least two departments. Its cost was minimal (below \$300.00) because existing materials from the AME Department were used wherever possible, and all my university fees were paid by the U.S. Air Force. It is intimately compatible with the HP 3052A computer data system, although that system remains mobile and available for other AME Department experiments. The reformer system can accurately control and evaluate the variables of temperature, pressure, flow rate and methanol/water ratio. The catalyst evaluation is easily done by overall results, but carbon buildup on the catalyst cannot yet be measured until the catalyst is removed. As discussed in the Carbon Detector section of Chapter 3, however, that problem should be solved with a few more runs.

5.2 Demonstrated Ability

The reformer system operation has demonstrated that at a methanol/water ratio of 1:1.3, an input flow of that solution at 5.81 liters per hour, and a catalyst bed temperature of 400°F, enough

hydrogen-rich carbon monoxide-poor product gas can be produced to power the fuel cell stack now under test by LASL at all but maximum power ratings. The size requirement for a redesigned reformer is small enough (1' x 1/2' x 1-1/2') that sufficient flow for maximum power could be developed by increasing the reformer catalyst volume or by increasing flow rate. At this point the reformer has been tested at an input flow rate as high as 9.4 liters per hour, but only at 600°F (Bertrand 1979). Conversion % (methanol to hydrogen) drops into the 60% range at rates above 6.0 liters per hour, but the unreformed methanol could be recycled. With either solution (more size or more flow) only modest changes are needed to meet all requirements imposed by the fuel cell stack currently under study.

CHAPTER 6

RECOMMENDATIONS

6.1 Gas Chromatograph

The only limitation on the data this system can provide is the sample analysis delay. The AME Department should install a gas chromatograph for near real time analysis of the product. Jim Blair has undertaken this project for his Master's Report.

6.2 Water Reduction

Further analysis of methanol/water ratio should be conducted once the carbon detector stabilizes. Reduction of the 1:1.3 ratio toward 1:1.0 will diminish the weight penalty of water if it can be done without carbon deposition on the catalyst.

6.3 Alcohol Funding

The U. S. Department of Energy is establishing an Office of Alcohol Technology. The AME Department should consider doing pioneering work with ethanol and use the leverage of having an operating reformer and doing advanced research to obtain funding from this new office to allow the work to be carried on full time.

6.4 Pressure Transducers

If the funds are granted, the pressure transducer panel should be designed and built because it appears the study of ethanol reformation will require higher pressures.

6.5 Optimum Size Reformer

If the funds are granted, a vehicle-size reformer should be built of optimum (rather than available) materials using the data provided by this system as a guide.

6.6 Fuel Cell Interface

If the funds and fuel cell are available, the fuel cell under consideration should be connected to this reformer output to overcome interface problems. Fuel cell liquid waste heat could then be tested as input heat to the redesigned reformer when it becomes available.

6.7 Government Policy

The United States should embark on an imaginative program of alcohol production from the available (coal) or renewable (grain, sugar, wastes) energy sources it possesses. The alcohol products can be mixed with current fuels (now done in many states), completely power vehicles as modifications and quantities allow, and eventually power fuel cell vehicles as petroleum based fuels disappear with consumption or political maneuvering.

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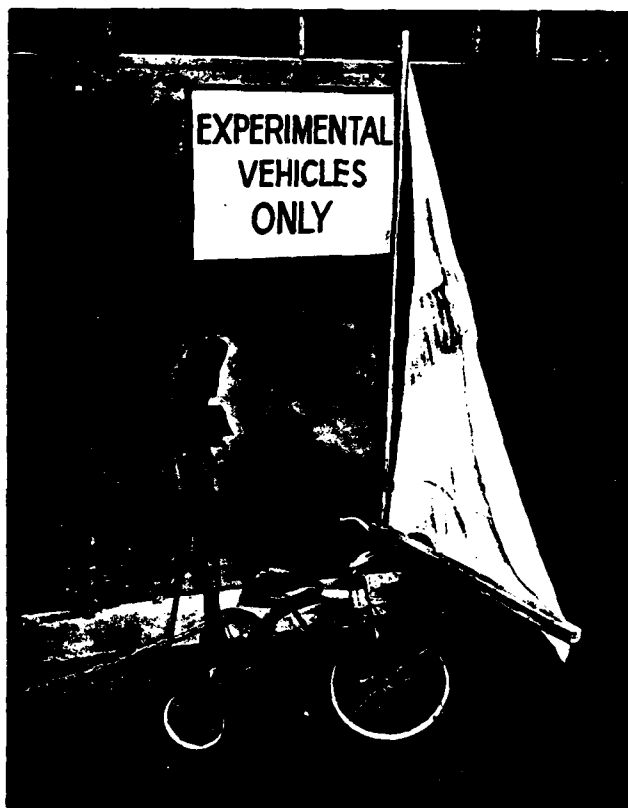
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APPENDIX A

HGO COMPUTER PROGRAM

```
10  OPTION BASE 1
20  DIM A$(25),Tpo(14)
30  FOR I=0 TO 9
40  A$(I+1)="CO"&VAL$(I)&"E"
50  NEXT I
60  FOR I=10 TO 24
70  A$(I+1)="C"&VAL$(I)&"E"
80  NEXT I
90  OUTPUT 722;"1R7T1M3A1H1"
100 PRINTER IS 16
110 INPUT "WAIT TIME=?",Zz
120 INPUT "WHICH DATA FILE,1-6,?",N
130 ASSIGN #1 TO "DATA"&VAL$(N)
140 BUFFER #1
150 Kk=1
160 PRINTER IS 10
170 PRINT "Station  Temperature,C  Temperature,F  Millivolts"
180 OUTPUT 9;"R"
190 ENTER 9;T$
200 PRINT T$
210 FOR I=1 TO 8
220 OUTPUT 709;A$(I)
230 WAIT Zz
240 ENTER 722;T1
250 OUTPUT 709;A$(14)
260 WAIT Zz
```

```
270     ENTER 722;T2
280     T=ABS(T1)+ABS(T2)
290     Tp=FNTemp(T)
300     Ta=1.8*Tp+32
310     PRINT I,Tp,Ta,T
320     Tpo(I)=Tp+273.16
330     NEXT I
340     FOR I=9 TO 13
350     OUTPUT 709;A$(I)
360     WAIT Zz
370     ENTER 722;T1
380     OUTPUT 709;A$(14)
390     WAIT Zz
400     ENTER 722;T2
410     T=ABS(T1)+ABS(T2)
420     Tp=FNTemp(T)
430     Ta=1.8*Tp+32
440     PRINT I,Tp,Ta,T
450     Tpo(I)=Tp+273.16
460     NEXT I
470     OUTPUT 709;A$(14)
480     WAIT Zz
490     ENTER 722;T
500     Tp=FNTemp(ABS(T))
510     Ta=1.8*Tp+32
520     PRINT "14",Tp,Ta,ABS(T)
530     Tpo(14)=Tp+273.16
540     PRINT #1,Kk;T$,Tpo(*)
550     Kk=Kk+1
560     IF Kk>=130 THEN 580
570     GOTO 180
580     PRINTER IS 16
590     INPUT "WOULD YOU LIKE TO RUN AGAIN ?",A$
```

```
600 IF (A$="YES") OR (A$="Y") THEN 90
610 END
620 DEF FNTemp(Voltage)
630 DIM Coeff(9)
640 K: !
650 Coeff(0)=.226584602
660 Coeff(1)=24152.109
670 Coeff(2)=67233.4248
680 Coeff(3)=2210340.682
690 Coeff(4)=-860963914.9
700 Coeff(5)=4.83506E10
710 Coeff(6)=-1.18452E12
720 Coeff(7)=1.3869E13
730 Coeff(8)=-6.33708E13
740 Temp=FNpoly8(Coeff(*),Voltage)
750 Rtn: RETURN Temp
760 DEF FNpoly8(Co(*),Val)=(((((((Co(8)*Val+Co(7))*Val+Co(6))
    *Val+Co(5))*Val+Co(4))*Val+Co(3))*Val+Co(2))*Val+Co
    (1))*Val+Co(0)
770 FNEND
```

APPENDIX B

THREE STANDARD PROCEDURES CHECKLISTS FOR SAFETY

Startup Checklist

1. Recommend having two or more people present at all times, never leave it unattended during a run.
2. Insure adequate supplies of the following are available:
 1. Unleaded gasoline
 2. Deionized water
 3. Methanol
 4. Recording notebooks
 5. Mixing glassware
 6. Stopwatch to time methanol/water consumption
 7. Sample bottles (gas and liquid) or supplies for chromatograph.
3. Insure all switches on control panel are off.
4. Start computer data system.
5. Check gasoline tank:
 1. Filled to just below air pressure inlet fitting
 2. Cap on snugly
 3. Pressure release valve closed
 4. Fuel line valve (to burner) open.

6. Turn on vent fan (SW corner).
7. Drain air compressor drain valve and dryer.
8. Open door from air compressor to hallway for cooling.
9. Drain air dryer in line to flowmeter panel.
10. Drain dryer in line to gasoline tank.
11. Open valve from evaporator to exhaust line.
12. Open air pressure valve to gasoline tank.
13. Set fuel pressure regulator to 9 psig (may require bleeding off pressure at tank pressure relief valve).
14. Turn on water to condenser and check float.
15. Open condenser drain line.
16. Open both main air line valves.
17. Set air line regulator pressure to indicate 40 psig on main flowmeter gage.
18. Close secondary air valve.
19. Adjust primary air valve to give 38-40%.
20. Turn on digital voltmeter with ohms and 10k selected.
21. Record initial DVM reading for carbon detector.
22. Turn on icepoint inside control panel.
23. Turn on igniter power supply and set at 24 volts.
24. Turn on igniter switch (make sure you hear it sparking).
25. Turn on readout switch.
26. Select Thermocouple #1 on readout.
27. Turn on Fuel Solenoid Switch.

28. Monitor Thermocouple #1:

1. Should hear a definite fuel "squirting" within 5 seconds.
2. Should see T1 indicate 1000°F or greater within 10-15 seconds.
3. Turn off solenoid switch if expected rise does not occur.

29. Record start time.

30. Allow a few minutes stabilizing time, then adjust primary air flow gradually toward full open (maintain T1 between 1100-1200°F).

31. Adjust fuel pressure as necessary, after 10 minute warmup, to maintain 1100-1200°F once primary air is full open.

32. Expected values for fuel and air settings, at steady state:

1. Fuel pressure: Range, 7-13 psig, 9-9.5 psig normal
2. Main air: 37-40 psig, 9-10%
3. Primary air: 49-53%.

33. Turn off igniter switch (leave igniter power supply on in case a flameout necessitates immediate use of the igniter).

34. Check P9 and P11 for pressure buildup inside the system. (Light process burner if necessary and open process outlet valve to reduce pressure.)

35. Adjust T1 to desired temperature with fuel pressure changes.

36. Run until sampling steady state is reached.

Sampling Checklist

1. Open natural gas line valve (near south wall).
2. Open process burner needle valve.
3. Light process burner.
4. Adjust to smallest flame necessary.
5. Close sample line valve at separator.
6. Open process output valve (on panel).
7. Turn on outlet power switch.
8. Mix methanol/water in desired ratio.
9. Set methanol/water consumption rate:
 1. Set pump speed with power supply controls.
 2. Set pump displacement with micrometer adjustment.
 3. Time methanol/water consumption on scale (1 cm = 3.82 ml).
10. Turn on hood vent fan (leave cover off to prevent switch over-heating which may automatically shutdown fan).
11. Expect product flame in 5-10 minutes or less.
12. Turn on vacuum pump switch.
13. Remove plugs and install gas sample bottle.
14. Open sample bottle valve.
15. Open vacuum pump line valve:
 1. Gage should show 25-30 psig vacuum.
16. Close vacuum pump line valve.
17. Open sample line valve at separator
18. Close sample line valve at separator when pressure is again positive.

19. Repeat steps 15 through 18 at least twice to remove all impurities from sample lines.
20. Establish sample parameters on system:
 1. Collect all condensate made prior to achieving the desired steady state.
 2. Insure T2 is at desired temperature.
 3. Adjust process outlet valve to achieve a positive pressure of 2-3 psig on P11 (Separator Output).
 4. Insure methanol/water mix is at desired flow rate and ratio.
21. Open vacuum pump line valve -- achieve 20-30 psig vacuum.
22. Close vacuum pump line valve.
23. Open sample line valve at separator.
24. Turn off vacuum pump switch.
25. Insure T9 (condenser output) is reasonably cool (75-90°F).
26. Adjust process outlet valve to achieve 5-10 psig on P11 so that cooling of the sample bottle will not put the contents below atmospheric pressure. WARNING: Do not completely close process valve because of hydrogen buildup.
27. Close sample bottle valve.
28. Close sample line valve.
29. Reduce P11 to 2-3 psig but do not open the process line valve abruptly or an excessively large process hydrogen flame may engulf you.

30. Stop methanol/water flow:

1. Turn off pump power supply.
2. Turn off outlet power switch.

31. Remove sample bottle carefully:

1. Do not loosen valve seal at bottle when loosening valve connection to tubing.
2. Install plugs in line and sample bottle.

32. Remove liquid condensate from receiver tank:

1. Open drain valve.
2. Collect and measure amount of condensate.
3. Measure condensate specific gravity on specially calibrated hydrometer.
4. Bottle and label small sample for analysis.
5. Close drain valve when flow stops.

Shutdown Checklist

1. Close air line valve to gasoline tank.
2. Close gasoline tank fuel outlet valve.
3. Bleed air pressure from gasoline tank.
4. Turn off fuel solenoid switch.
5. Turn off igniter switch.
6. Turn off igniter power supply.
7. Monitor T1 for temperature dropoff
8. Turn off ice point.
9. Turn off DVM
10. Close both main air line valves.

11. Close cooling water valve.
12. Turn off SW corner vent fan.
13. Allow process hydrogen flame to burn out.
14. Close process line outlet valve.
15. Close process burner natural gas valve.
16. Close natural gas line valve (S side of building).
17. Close exhaust line valve.
18. Turn off hood vent fan -- carefully replace cover first.
19. Turn off all control panel switches.
20. Shutdown HP computer data system.
21. Clean up glassware.

LIST OF REFERENCES

- Baker, Bernard S. "Fuel Cells for Automotive Power Plants," Proceedings of the Fuel Cell in Transportation Applications Workshop, Los Alamos Scientific Laboratory, August 15-17, 1977.
- Bertrand, Louis. "Unpublished Notebooks on Methanol Reformation," The University of Arizona, 1979.
- Dawkins, Daniel B. Hydrocarbon Reforming for Hydrogen Fuel Cells, DOE Program Research and Development Announcement Number DE-RA21-79MC11323, Morgantown, West Virginia, May 23, 1979.
- Dixon, A. G., A. C. Houston and J. K. Johnson. "An Automatic Generator for the Production of Pure Hydrogen from Methanol," paper presented to the Seventh Intersociety Energy Conversion Engineering Conference, San Diego, California, September 25-29, 1972.
- Farmer, M. H. "Feasibility of Automotive Fuels from Coal and Oil Shale," paper presented at the Tenth Intersociety Energy Conversion Engineering Conference, Newark, Delaware, August 17-22, 1975.
- Francis, Devon. "A Hydrogen Engine That Looks Practical," Mechanix Illustrated, July 1977, p. 42.
- Gillis, Edward A., O. Fred Kezer, Jr. and Walter G. Taschek. Open Cycle Hydrocarbon-air Fuel Cell Power Plant, Army Mobility Equipment R & D Center, Fort Belvoir, Virginia, 1970.
- Gillis, J. C., J. B. Pangborn and K. C. Vyas. "The Technical and Economic Feasibility of Some Alternative Fuels for Automotive Transportation," paper presented at Tenth Intersociety Energy Conversion Engineering Conference, Newark, Delaware, August 17-22, 1975.
- Gonnerman, C. H., J. S. Moore and P. W. McCallum. "Fueling Automotive Internal Combustion Engines with Methanol -- Historical Development and Current State of the Art," paper presented at the Tenth Intersociety Energy Conversion Engineering Conference, Newark, Delaware, August 17-22, 1975.

- Hoover, D. Q. Third Quarterly Report on Cell and Stack Design Alternatives, prepared for DOE for the period February 1, 1979 -- April 30, 1979, under contract DE-AC03-78ET11300, by Westinghouse R & D Center, Pittsburgh, Pennsylvania, May 1979.
- Hyde, Susan. "Unpublished Notes for Master's Report on Thermodynamic Analysis of Aerospace and Mechanical Engineering Department's Reformer System," The University of Arizona, 1979.
- Kerwin, William L. "Unpublished Notes on Fuel Cell Test," Los Alamos Scientific Laboratory, June 5, 1979.
- Kester, Frank L., Alex J. Konopka and Elias H. Camara. "Automotive Hydrogen Storage Feasibility -- Methanol Steam Reforming," paper presented at ERDA Advanced Automotive Power Systems Division Contractors' Coordination Meeting, Ann Arbor, Michigan, May 6-8, 1975a.
- _____. "On Board Steam Reforming of Methanol to Fuel the Automotive Hydrogen Engine," paper presented at the Tenth Intersociety Energy Conversion Engineering Conference, Newark, Delaware, August 17-22, 1975b.
- _____. Final Report on Automotive Storage of Hydrogen as a Mixture of Methanol and Water, prepared for the EPA under contract 68-03-2057 by the Institute of Gas Technology, Chicago, Illinois, November 1975c.
- Kurpit, Stanley S. "1.5 and 3 KW Indirect Methanol-air Fuel Cell Power Plants," paper presented at the Tenth Intersociety Energy Conversion Engineering Conference, Newark, Delaware, August 17-22, 1975.
- Lawrence, L. R. ERDA National Fuel Cell Program Category Plan, ERDA, Washington, June 18, 1976.
- _____. "The ERDA Fuel Cell Program," Proceedings of the Fuel Cell in Transportation Applications Workshop, Los Alamos Scientific Laboratory, August 15-17, 1977.
- Lorton, Gregory A. Steam-hydrocarbon Reforming for Lower Polluting Automotive Fuels, Thesis submitted to Department of Chemical Engineering, The University of Arizona, 1973.
- Martin, Marvin D. A Research Proposal: Use of Waste Heat for Steam Reformation of Hydrocarbon Fuels in Internal Combustion Engines, The University of Arizona, Department of Aerospace and Mechanical Engineering, 1977.

McCormick, Byron. "Welcoming Address," Proceedings of the Fuel Cell in Transportation Applications Workshop, Los Alamos Scientific Laboratory, August 15-17, 1977.

NASA, Background Information on Fuel Cells, prepared for ERDA, July 1975.

Omega Engineering, Temperature Measurement Handbook, Omega Engineering, Stamford, Connecticut, 1972.

_____. Electronic Icepoint Manual: Model MCJ, Omega Engineering, Stamford, Connecticut, 1977.

Prigent, M., C. Dezael and Y. Breelle. "Technology of Pure Hydrogen Generators Using Methanol and the New Application Prospects They Create for Hydrogen-air Cells," paper presented at the Fifth Intersociety Energy Conversion Engineering Conference, 1970.

Reed, T. B. and R. M. Lerner. "Methanol: A Versatile Fuel for Immediate Use," Science, December 28, 1973, pp. 1300-1302.

Scott, Lawrence B. Jr. Reforming Liquid Hydrocarbons to Produce Synthetic Gas (Summary Proposal Draft), Aerospace and Mechanical Engineering Department, The University of Arizona, 1979.

Stinson, Stephen C. "Methanol Primed for Future Energy Role," C & EN, April 2, 1979, p. 28.

Walsh, Edward M. Energy Conversion, Ronald Press, New York, 1967.

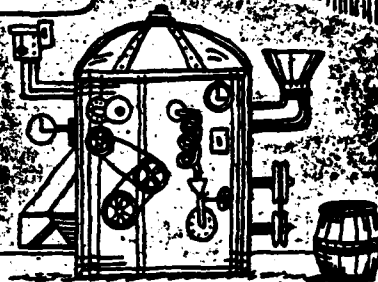
Wilk, A. S. "Final Report on Task 008," Plan for the Development of Fuel Processors for Fuel Cell Systems, Prepared for DOE under contract EF-77-C-01-2468, by the Engineering Societies Commission on Energy, Washington, November 1978.

Willan, Vernon O. Development of a Supplemental Heater for Use on a Steam-hydrocarbon Reforming Reactor, report prepared for the National Science Foundation and Aerospace and Mechanical Engineering Department, The University of Arizona, Summer 1977.

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